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PRINCIPLES OF EXPERIMENTAL AND THEORETICAL ELECTROCHEMISTRY

PRINCIPLES OF EXPERIMENTAL AND THEORETICAL ELECTROCHEMISTRY

By

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PREFACE

It is the purpose of this text to describe the science of electrochemistry from a viewpoint somewhat different from the viewpoint of older electrochemical texts. Electrochemistry has been defined* as that part of chemistry which is "mainly concerned with the interconversion of electrical and chemical forms of energy," but this definition is too vague and too general for modern science, inasmuch as *all* chemical reactions and chemical phenomena are now being interpreted on the basis of electrical attractions, repulsions, or interactions. Indeed, it is beginning to be doubtful if there is any form of chemical energy which is not essentially electrical energy, if there is any chemical phenomenon whose origin cannot be traced to an electrical effect. If this older definition of electrochemistry were adopted, we could include in our text the description of practically any chemical phenomena whatsoever without being inconsistent; for this reason a new and more restrictive definition of electrochemistry is necessary.

The science of electrochemistry is defined here as the organized body of chemical knowledge that has been accumulated through the application of electrical current or electric (or magnetic) fields in the solution of chemical problems, and through the measurement of electric currents or electric potentials flowing through or generated by chemical cells. This new definition lays stress on the experimental side of electrochemistry; the study of electrochemistry must begin, therefore, with a description of the electrical apparatus and methods employed, followed by a theoretical interpretation of the data so electrically obtained. The selection of the material for this book has been made with this definition in mind and some of the subject matter of older electrochemical texts such as theories of indicators, of neutralization, of buffer solutions, of solubility, of colligative properties of solutions, etc., have not been mentioned or have been only

* S. Glasstone, "The Electrochemistry of Solutions," Methuen and Co., London, 1930.

briefly discussed, since they are considered to be outside the domain of electrochemistry as defined above. On the other hand, our new definition of electrochemistry brings into this science such interesting fields as dielectric-constant and electric-moment measurements, molecular-ray experiments, high-frequency and high-voltage conductance phenomena, electrokinetic and electrocapillary phenomena, and phase-boundary and semipermeable membrane potentials, etc., electrical effects which have been omitted or perhaps only lightly touched upon in other electrochemical texts. However, it has been found necessary to include a condensed discussion of certain subjects such as Fundamentals of Thermodynamics (Chap. XV) that, while in no sense a part of electrochemistry by our new definition, must be presented in order to clarify the strictly electrochemical subject matter treated later in the book.

There are, of course, other principles which have been considered in composing this textbook, the most important of which was the advisability or perhaps necessity of including material suited to and needed by the class of student for whom this book is written, namely, graduate students in chemistry who have already had an elementary course in physical chemistry. The subject matter of other electrochemical texts has been helpful in suggesting material as has been a consideration of electrical experiments now in progress in physical chemical laboratories in universities throughout the world.

It is rather natural for one who has devoted a large part of his scientific life to experimental electrochemistry to discuss electrochemistry from an experimental angle and to include in the textbook chapters dealing solely with experimental technique and methods. The experimental matter, however, is largely set off in chapters by itself so that it may be omitted if of no interest to the reader.

In defense of the nomenclature adopted in this text, it may be said that no new symbols have been introduced as far as the author is aware, most of the symbols adopted being in general use either in this country or abroad. The thermodynamic conventions and symbols follow for the most part those of Guggenheim as given in his new treatise "Modern Thermodynamics by the Methods of Willard Gibbs." The symbol G is

used for free energy instead of the more usual F because of the nuisance occasioned by the necessity of distinguishing between F meaning the faraday and F meaning free energy when writing equations such as $\Delta F = -nFE$ on the blackboard. Guggenheim and Schottky, Ulich and Wagner in their thermodynamic treatises use G meaning free energy also. The sign conventions follow Getman and Daniels except that emphasis is placed on direction of positive current flow in the cell and positive potential rather than on electron pressure and electron flow.

Grateful acknowledgments are due Professor Grinnell Jones, of Harvard University, and Professor Frank T. Gucker, Jr., of Northwestern University, who have read parts of the text and have offered helpful suggestions. The typing and checking of references were ably done by the Northwestern undergraduates, Aileen Schoeppe, Thelma Salisbury, and Agnes Andersen working on a FERA grant from the Government while Charlotte Erwin and B. Z. Wiener, graduate students at Northwestern University, generously aided in the proofreading.

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MALCOLM DOLE.

EVANSTON, ILLINOIS.

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PRINCIPLES OF EXPERIMENTAL AND THEORETICAL ELECTROCHEMISTRY

CHAPTER I

HISTORICAL INTRODUCTION

Prior to the discovery of the voltaic pile in 1800 it was well-nigh impossible to produce measurable electrochemical effects because electric currents of appreciable magnitude were unobtainable. Of necessity, therefore, there were no great discoveries in the field of electrochemistry during most of the eighteenth century. It is true that at an early date Pater Beccaria obtained mercury from cinnabar by reducing the oxide in the spark from two Leyden jars, and Priestley, in 1775, formed an acid by discharging electricity through ordinary air, an acid which Cavendish later demonstrated to be nitric acid, but these experiments were of the nature of isolated observations and did not lead to any general advance in the field of electrochemistry. Paets van Troostwijk and Deimann decomposed water in 1789 and found that the longer a spark passed between the electrodes in the water, the more gas they obtained. On exploding the resulting gas mixture water was again formed leaving no appreciable residual gas. As an example of the difficulty which these early scientists encountered in obtaining electrochemical effects even on a laboratory scale, we can quote the results of Pearson who in 1799 reported that in the decomposition of water 14,600 discharges of his Leyden jars were needed to give $\frac{1}{3}$ cu. in. of gas. Needless to say nothing at all was understood concerning the action of the electricity in bringing about these effects, no generalizations were made, and no fundamental theories were advanced.

However, toward the close of the eighteenth century a most remarkable observation was made by Galvani who in 1791

performed his famous frog's leg experiment, an experiment which tremendously excited the whole European scientific world and which led to further experiments of the greatest electrochemical consequences. In a paper entitled *Aloysii Galvani de Viribus Electricitatis in Motu Musculari Commentarius, Bononiae* 1791 Galvani wrote as follows. "If I held a previously prepared frog with one hand by a metal (iron) hook, which was inserted into the spinal marrow, so that the feet of the frog touched a silver bowl and if with the other hand I held a metal rod which touched the silver bowl on which the frog's legs rested, the frog's legs jerked violently contrary to all our expectations and indeed this happened as often as I made use of this artifice." Further, "If a frog is held by one leg so that the metal hook sunk into the spinal marrow touches a silver disk and so that the other leg falls freely onto the disk, it happens that as the free leg touches the silver surface, the muscles immediately contract and the leg of the frog rises. However, the leg will begin to fall again and when it touches the silver disk the second time, the leg will again rise and so it will continue to rise and fall, thus appearing to the astonished and amused investigator to be an electrical pendulum."

Galvani was chiefly interested in the biological and medical aspects of his discoveries; he believed in an animal electricity and considered the two different metals which completed the leg-nerve-hook-metal-leg circuit as of importance only in allowing the electricity to flow from the leg to the nerve. Although the physiological relations between muscle action, electric shock, electric currents, and life processes are exceedingly interesting and fascinating and to this day continue to challenge the imagination of man, their study and description are beyond the scope of this book; hence we shall not consider further the numerous and varied experiments which Galvani carried out with his frog's legs but will pass on to the work of Volta, who in an inspired moment cast rather scornfully all Galvani's ideas of animal electricity aside and concentrated attention on the metallic part of Galvani's frog's leg circuit.

At this point it should be remarked that Galvani's discovery in addition to stimulating research along electrochemical lines also provided scientists with a method of detecting very small electric potentials. To contract the muscles of an uninjured

frog a voltage equal to four or five degrees of the Henley quadrant electrometer (in use at that time) was needed. If its head was cut off and a needle thrust into the spinal marrow, a voltage equal to one or two degrees was needed. If the frog was dissected so that the spinal marrow hung to the legs only through the crural nerves, the legs became sensitive to a voltage which could actuate only the most sensitive electrometers of Galvani's period, and finally if the nerves were covered with tin foil, the legs reacted to a voltage smaller than could be detected by the finest of the old electrometers.

Volta, a physicist, believed that the frog's legs acted similarly to an electroscope and he was interested in the kicks of the legs only insofar as these jerks indicated the presence of electric potentials. He did not try to understand as Galvani did why the legs kicked. In 1792, Volta pointed out that the cause of the jerks could be traced to the presence of two different types of metals in the circuit. Galvani had found that if the nerve-frog-leg circuit was closed by a conductor made exclusively of one metal, no contractions of the frog's legs occurred; the metallic connection had always to be composed of two different metals. Volta's instinct led him unerringly to consider this surprising experimental fact as the outstanding discovery among the wealth of observations accumulated by Galvani. Volta believed that the electricity which actuated the frog's legs arose *at the junction of the two unlike metals;* in order to verify and confirm his ideas he studied the effects produced on the frog's legs by many combinations of metals and from these studies he was able to list the metals in the order of their effectiveness. This list or series of metals was the forerunner of, and, in fact, remarkably similar to, the well-known "e.m.f. series of metals" of today. Published in November, 1792, Volta's series ran zinc, tin foil, ordinary tin foil in the form of plates, lead, iron, brass, bronze, copper, platinum, gold, silver, mercury and graphite. Volta also showed that different liquids in contact would produce the same effect, although the effect was much weaker than that produced by metals.

For several years after 1792, Volta contributed no publications, but he was continuing his experiments as we shall see shortly.

Meanwhile a significant advance was made by the German investigator, Ritter, who first pointed out that Volta's series

of the metals agreed with the series of metals one would get if the metals were arranged in the order of their chemical activity. Ritter also performed a valuable service to electrochemistry when in his paper entitled *Auch in der anorganischen Natur ist der Galvanismus wirksam,* he brought the problem from the special field of physiology over into the domain of physical chemistry.

Up to this point in the development of electrochemistry the electrical currents available to scientists arose in two ways: they were either very small currents associated with high potentials or they were fairly significant currents associated with small voltages. With neither of these two sources of electricity could results of any great electrochemical interest be obtained. As mentioned before, infinitesimal electric currents produce undetectable effects. Furthermore, large currents are practically useless if the available voltage is small. As we shall learn in a later chapter a voltage of 1.7 is necessary for the decomposition of water; voltages under this value are usually too small to decompose substances or to overcome the polarization of cells. What was needed to initiate the new science of electrochemistry was a source of electricity producing large voltages and large currents. At the beginning of the nineteenth century the scientific world of Europe was ready and waiting for such a source; the time was ripe for its discovery.

With the birth of the new century came the invention of the "voltaic pile," a discovery to which we can rightfully attribute the birth of electrochemistry. Volta first described his pile or battery in a letter dated Mar. 20, 1800 to President Banks of the Royal Society of London. In this letter he showed how the electric current which arose at the junction of two unlike metals could be intensified by joining several pairs of these metals together in such a way that one metal alternated with another metal, the connections between the two metals being, first, a metallic connection and, second, a wet or liquid connection. Speaking in modern terminology we can say that Volta discovered the secret of multiplying the voltage of a battery by connecting his cells together in *series*. In other words he obtained a summation of the voltage of the separate cells. Actually Volta formed his pile by piling layers of metals and moistened paper on top of each other. Thus his layers in the form of disks ran, for example,

copper, moistened paper, zinc, copper, moistened paper, zinc, copper, etc. There is no doubt that Volta was able to obtain quite large currents from his pile and that the available voltage was more than sufficient to carry out many types of electrochemical reactions. Volta also made the following interesting observations: He found that the metal plates need touch only in a few places, but that the damp layer in between the disks must everywhere be in good contact. Volta recognized that positive and negative potentials existed in his pile, that the salt concentration of the damp layer and the temperature of the pile influenced the intensity of current, that placing a foreign metal between the copper and zinc disks had no effect, that a current divides itself between conductors placed in parallel (this fact partially anticipates Ohm's law), and that there is a significant difference between conductors of the first and second class, *i.e.*, metallic and electrolytic conductors.

It is interesting to note that Volta believed that he had discovered a perpetual-motion machine. He thought that the tendency of the current from his pile to diminish in intensity with time was due to the drying out of his moistened paper layers. Volta knew nothing of the chemical reactions which occurred within his pile nor did he think to perform with the current from his pile external chemical reactions. Nevertheless, his discovery places him eternally in the front rank of great scientists.

Other workers were quick to use Volta's pile in chemistry. Even before Volta's letter to Banks was published, Nicholson and Carlisle who had heard of his invention were applying the current from his pile to decompose water. Using platinum electrodes they proved the evolution of hydrogen and oxygen. They also demonstrated the formation of acid and alkali in the electrolyte around the platinum points. Davy, however, was the first to decompose water quantitatively. This was also done later by the German, Ritter, who was unaware of the work of the Englishmen. In 1800, the year of the publication of Volta's discovery, we also find Cruikshank depositing lead from lead acetate and forming silver chloride on silver electrolytically.

Perhaps the most brilliant experiment of this decade and one which caused a great sensation was the decomposition of caustic potash into its elements by Davy in 1807. Although the dis-

covery of the alkali metals was very important for chemistry, it did not add anything particularly fundamental to the content of electrochemistry. Using platinum-tipped wires Davy applied a current from a voltaic pile composed of 250 pairs of plates to the dry solid base. The heat generated by the current melted the base which then became conducting; the little globules of potassium caught fire at the cathode as rapidly as they were formed, some of them exploded and flew through the air with great speed, the incessant production of sparks and fire being a very startling sight. The isolation of the other alkali metals soon followed and later Berzelius was able in this way to discover barium.

Ideas concerning the mechanism by which the electric current is transmitted through the electrolyte were not lacking. Grothuss at the age of twenty published in 1806 a theory of conduction which was believed to be correct by scientists for a great many years, a theory, moreover, which, dressed up in the language of wave mechanics, has recently been used by Bernal and Fowler to explain the abnormally high mobility of the hydrogen and hydroxyl ions. Grothuss explained his theory in this way: "Consider a certain amount of water which consists of oxygen designated by a negative sign (−) and of hydrogen designated by a positive sign (+). The moment a current flows through the cell the electrical polarity between the atoms becomes valid so that these represent a complement of the actual pile. At the same time all the oxygen atoms which find themselves in the path of the current have a tendency to move toward the positive pole while all the hydrogen atoms lying in the same path will tend to seek the negative pole." If we describe the theory of Grothuss in modern terminology, we say that Grothuss postulates the existence of charged atoms or ions, but that these ions exist only during the passage of electricity through the cell. Furthermore, these ions do not exist independently of each other even during the passage of the current, but rather are passed along from one molecule to the next as the electricity flows through the cell. This type of conduction is sometimes called the "Grothuss chain conduction."

Between the time of Davy and Grothuss and that of Faraday and even later many erroneous ideas and misinterpreted data were

published by electrochemists. In his monumental history of electrochemistry Ostwald devotes considerable space to these "galvanic phantasies," as he calls them, but here we shall pass over them with the sole comment that undoubtedly many of these fantastic results were not without some beneficial influence on the development of electrochemistry.

Modern electrochemistry may be said to have begun with the discovery by Faraday of the fundamental laws that bear his name and with the introduction into electrochemistry of the terminology invented by him. These important developments of electrochemistry are fully described elsewhere in this book as are also later discoveries and inventions; hence we shall terminate our brief historical survey of electrochemistry at this point and shall pass over to the consideration of one of the most fruitful ideas that has ever been introduced into electrochemistry, *viz.*, the Arrhenius theory of dissociation.

CHAPTER II

THE ARRHENIUS DISSOCIATION THEORY

(See Appendix I for a list and meaning of symbols used throughout the book.)

The most important concept in electrochemistry is undoubtedly the theory of the existence of charged particles or ions in solution. It is perhaps no exaggeration to say that very little of this book could have been written if the use of ions in describing and explaining the observed phenomena were denied us. It is essential, therefore, that the facts and observations upon which the ionic theory is based are thoroughly understood before proceeding with our study of electrochemistry.

As remarked in the last chapter the Grothuss chain theory of electrical conduction in solutions held sway for a great many years, but slowly new experiments were performed and new data accumulated which could not be explained by this theory. Buff proved that an infinitesimally small voltage was able to produce an electric current in the solution. If decomposition of the neutral molecules in the solution into electrically charged ions is brought about solely by the electric current, it would seem reasonable to suppose that the application of a definite potential difference would be necessary to decompose the dissolved molecules, and any value of the applied potential below this minimum would result in no decomposition and no current. The fact that this was not so, that the smallest possible voltages could produce a current, seemed to indicate that whatever carried the electric current through the solution was not produced by the current itself. Clausius tried to explain electrolytic conduction by assuming that certain of the solute molecules would be traveling at such high speeds through the solution that they would be dissociated into ions in much the same way that gas molecules become dissociated when heated to a sufficiently high temperature. Unfortunately for this theory, the number of such

dissociated molecules was shown to be too small at room temperature to account quantitatively for the observed effects.

Facts gleaned in the study of chemical reactions carried out in solution must have been very puzzling without the ionic theory to explain them. It was observed that mixing two salt solutions produced no thermal effect, a surprising and entirely inexplicable result. Furthermore, the heat of neutralization of sodium hydroxide with hydrochloric acid was found to be almost exactly the same as the heat of neutralization of potassium hydroxide with hydrochloric acid, although the formation of two different salts would seem to necessitate the production of different amounts of heat. Before the theory of Arrhenius there was no good explanation for the difference in the rate of inorganic and organic reactions nor for such interesting facts as the ability of silver nitrate to precipitate silver chloride from some solutions containing the element chlorine and not from others. A difference was noted between "acidity" of solutions and total acid present, but this difference was little understood.

The need for a sound theory of electrolytic solutions was evident in the attempts of early electrochemists to explain the voltages of e.m.f. (electromotive force) cells. So little did the first workers in this field understand the mechanism by which the cell potentials are produced that in writing down their cells in their published articles they considered it unnecessary to include the electrodes!

It occurred to Arrhenius while engaged in measuring the electrical conductance of acid solutions for his doctor's thesis to compare the conductance of acids with their chemical behavior. He found that a definite correlation existed between these two properties; if the acid was a strong acid, it conducted the electrical current well, while if it was a weak acid, it conducted the current poorly. Since this correlation seemed to be quite general, Arrhenius concluded that the agent in the solutions which was active chemically and active in conducting the current must actually be the same agent in both cases. From this important idea, it was a simple step for Arrhenius to assume that the agent which makes a solution conducting must really exist before the current flows through the solution. According to Arrhenius a finite voltage was not necessary to decompose the solute molecule

and to make the solution conducting because the charged ions existed in the solution even before the external voltage was applied. The salt became "ionized" or "dissociated" the moment it dissolved. In this way Arrhenius solved the problem of accounting for the existence of ions and overcame the difficulties which the experiments of Buff had given to the Grothuss theory.

Now Arrhenius did not stipulate that all the solute molecules were dissociated in solution, for he realized that some acids conducted the current well and some poorly. His idea was that the strength of acids was to be explained on the basis of the number of dissociated solute molecules. If the molecules were nearly all dissociated, the acid was strong and conducted the current well, but if only a small fraction of the solute molecules was dissociated, the acid was weak and conducted the current poorly. Arrhenius introduced a quantity, α, called the "degree of dissociation," defined by the equation:

$$\alpha = \frac{\text{number of solute molecules dissociated}}{\text{total number of solute molecules before dissociation}}. \tag{1}$$

The fraction of molecules ionized, α, is an important quantity in the Arrhenius theory because it is a measure of the number of ions present. If the electrolyte has the concentration c moles per liter of solution, the concentration of the ions will be αc moles per liter for each ion that results on dissociation of the molecule. For example, $0.001c$ acetic acid is 12.38 per cent dissociated, α equal to 0.1238, and the concentration of the hydrogen ion is equal to 0.001×0.1238 or 0.0001238 mole per liter. The concentration of the acetate ion is also 0.0001238 mole per liter. In the case of dibasic acids, such as sulfurous acid, it is customary to treat each of the two possible dissociations in the same way that the single dissociation of a monobasic acid is treated; but it is necessary to add to the concentration of the hydrogen ions resulting from the first dissociation the concentration of the hydrogen ions resulting from the second dissociation in order to obtain the total hydrogen ion concentration of the solution. (The hydrogen ions resulting from the dissociation of water must also be considered in certain cases.)

Arrhenius believed that the dissociation of acids (and bases and salts also) was a chemical reaction in which equilibrium between the dissociated and undissociated particles was attained. For the dissociation of the acid, HA, for example, the equilibrium could be written

$$HA \rightleftarrows H^+ + A^-. \tag{2}$$

Arrhenius also believed that the degree of dissociation was a function of the concentration. In dilute solutions the solute would be nearly all in the dissociated state, but as the solution became more concentrated, the degree of dissociation would become less. This last assumption is in agreement with many facts which we know concerning solutions, in particular Arrhenius introduced this assumption to account for the change of equivalent conductance (a quantity related to the degree of dissociation) with change of concentration.

From its very beginning Arrhenius's theory has had great success in explaining phenomena observed in the case of electrolytic solutions. From a quantitative standpoint his theory was first tested by applying the mass action law to equilibrium (2) obtaining the equation

$$K_c = \frac{c_{H^+}c_{A^-}}{c_{HA}}, \tag{3}$$

where K_c is the so-called "dissociation constant" and c refers to concentration in moles per liter. Since $c_{H^+} = c_{A^-} = c\alpha$ and $c_{HA} = (1 - \alpha)c$, Eq. (3) may also be written

$$K_c = \frac{\alpha^2 c}{1 - \alpha}, \tag{4}$$

where c is the stoichiometrical concentration of the solution. If α can be measured, K_c may readily be calculated from Eq. (4). Historically, Arrhenius first determined α from conductance data for acetic acid solutions (Chap. V) and then calculated K_c over a range of concentrations which he found to be constant. Table I gives some values for the dissociation constant of acetic acid calculated by MacInnes and Shedlovsky* from their accurate conductance data. This calculation is quite involved and

* D. A. MacInnes and T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1429, (1932).

includes two modifications which have been shown to be necessary within the last ten or twenty years. We shall not be prepared to study this new method of calculation until the Lewis activity concept and the Debye and Hückel correction to the Arrhenius theory have been described; hence at this point we shall merely give the data as an illustration of the successful application of the Arrhenius theory, reserving the detailed discussion of the method of calculating K until a later chapter.

TABLE I.—DISSOCIATION CONSTANT OF ACETIC ACID AT 25°C.

Concn. $c \times 10^3$	$K \times 10^5$
0.028014	1.752
0.11135	1.754
0.15321	1.750
0.21844	1.751
1.02831	1.751
1.36340	1.753
2.41400	1.750
3.44065	1.750
5.91153	1.749
9.8421	1.747
12.829	1.743
20.000	1.738
50.000	1.721
52.303	1.723
100.00	1.695
119.447	1.689
200.00	1.645
230.785	1.633

In the dilute solution range the constancy of K is all that can be desired, but above a concentration of 0.01 N disturbing influences begin to be felt and K begins to decline in magnitude. At this point it should be noted that a dissociation constant K can only be calculated for those substances whose degree of dissociation varies fairly considerably with the concentration. Thus, a similar calculation for potassium chloride would not yield constant values for K. The reason for this will be considered later.

Arrhenius's theory was immediately successful in explaining the anomalous results obtained by van't Hoff in his work on osmotic pressure and other colligative properties such as the freezing point lowering. Van't Hoff had discovered that Avogadro's law could be applied to solutions of nonelectrolytes;

i.e., he discovered that a dissolved substance produced in solution an osmotic pressure equal to the pressure the substance would produce if it were a gas at the same temperature and volume. Calculations of the gas constant, R, from osmotic pressure data gave practically the correct value. However, there were many solutions for which Avogadro's law seemed not to be valid. Avogadro's law as applied to solutions states that the same number of dissolved particles of any substance at the same temperature and volume will produce the same osmotic pressure. But van't Hoff found that this was not true for electrolytic solutions, the osmotic pressure of these solutions being considerably greater than that calculated on the basis of Avogadro's law. For a normal solution the osmotic pressure is given by the equation

$$P_oV_o = RT, \tag{5}$$

where P_o is the osmotic pressure, V_o the volume of solution containing one mole, T the absolute temperature, and R the gas constant. In order to bring Eq. (5) into agreement with the data for abnormal solutions, van't Hoff introduced the empirical factor, i, obtaining the equation,

$$PV_o = iRT. \tag{6}$$

By comparing Eq. (6) with the perfect gas law equation

$$PV = nRT \tag{7}$$

it is apparent that i bears some relation to the number of moles in the solution. The van't Hoff factor i is also equal to the ratio of the freezing point lowerings of the abnormal and normal solution as well as to the ratio of the osmotic pressures, the relationships being

$$i = \frac{P}{P_o} = \frac{\Delta tf}{(\Delta tf)_o}, \tag{8}$$

where P and Δtf represent the osmotic pressure and freezing point lowering of the abnormal solution and P_o and $(\Delta tf)_o$ similar quantities for the normal solution. The van't Hoff factor i is particularly suited to measure the deviation of solutions from Avogadro's laws; any value of i different from unity is, of course,

abnormal. Table II includes some representative values of taken from the recent monograph published by Falkenhagen.*

TABLE II.—VALUES OF THE VAN'T HOFF FACTOR i FROM FREEZING POINT LOWERINGS

m^a	i	m^a	i
KCl		$BaCl_2$	
0.001	1.97	0.000214	2.99
0.005	1.96	0.000872	2.86
0.01	1.94	0.00273	2.83
0.0497	1.91	0.01142	2.72
0.0867	1.86	0.11358	2.52
$La(NO_3)_3$		CH_3COOH	
0.00132	3.75	0.00952	1.10
0.00354	3.56	0.003007	1.08
0.00806	3.40	0.01002	1.054
0.0177	3.12	0.03535	1.04
0.0430	2.96	0.0951	1.02

m^a = (moles per 1,000 g. of water).

Van't Hoff was unable to explain the abnormally high values of i, but on the basis of the Arrhenius theory they were readily understandable. For some time previous to the Arrhenius theory, it had been known that certain gases such as ammonium chloride gave abnormally high gas pressures. The apparent deviation of these gases from Avogadro's law was explained on the assumption of dissociation; thus, ammonium chloride gave too high a gas pressure because it was partially dissociated into ammonia and hydrogen chloride. It was only natural for Arrhenius to explain the abnormal osmotic pressures of solutions in the same way. Potassium chloride solutions had twice the osmotic pressure expected, van't Hoff factor equal to 2, because each molecule of the salt dissociated into two ions giving twice the number of dissolved particles and therefore twice the osmotic pressure. Similarly, each molecule of barium chloride dissociated into three ions, lanthanum nitrate molecules into four ions and

* H. FALKENHAGEN, "Elektrolyte," p. 26, Leipzig, 1932.

the osmotic pressure of barium chloride solutions was three times as great as calculated and that of lanthanum nitrate four times as great. In the case of acetic acid which is very little dissociated at the concentrations listed the van't Hoff factor is only slightly greater than unity.

It is possible to write down the relationship between the van't Hoff factor i and the Arrhenius degree of dissociation, α. The latter is a measure of the number of ions in the solution, but i is a function of the number of all the particles, ionized or unionized, that are dissolved in the solution. The total number of moles in a liter of solution of a salt whose molecules ionize into n ions each is equal to

$$(1 - \alpha)c + n\alpha c, \tag{9}$$

but the number per mole of dissolved solute is

$$1 + (n - 1)\alpha. \tag{10}$$

The quantity, Eq. (10), is equal to i,

$$i = 1 + (n - 1)\alpha, \tag{11}$$

since i represents the number of moles of solute particles per mole of dissolved solute.

Arrhenius's theory was even more successful in its application to the chemistry of inorganic solutions. Reactions in solution which are now called ionic reactions proceed with great and almost instantaneous velocity in contrast to reactions between organic molecules. The difference in the rates of reactions between inorganic and organic substances depends upon the difference in the number of activated molecules present in the two cases. Arrhenius's theory of reaction rates,* which has been amply verified as far as its fundamental postulates are concerned, attributes the speed of reactions to the number of activated molecules available for combination, no reaction between unactivated molecules being possible. Activated molecules are those containing an excess of energy, molecules in which the electrons are in higher than normal energy levels, for example. Ions are molecules which may be considered as being highly activated; the electron has been completely removed from the ion in the case of positive ions and given to the ion in the case of

* Not to be confused with his electrolytic dissociation theory.

negative ions. In electrolytic solutions there are great numbers of these activated molecules, the ions, and the speed of reaction is, therefore, almost instantaneous. In solutions of organic substances only a small fraction of the dissolved molecules are activated; therefore the reactions take place comparatively slowly. In this way does the Arrhenius theory explain the difference between the rate of reactions in inorganic and in organic solutions. The ability of silver nitrate to precipitate silver chloride from potassium chloride solutions, but not from potassium chlorate solutions, is due to the fact that the silver ion combines with the chloride ion in the first case, but cannot combine with the chlorine in potassium chlorate because the chlorine is in the chlorate ion. This is the explanation given by the Arrhenius theory. Similarly, chlorine combined in organic compounds in such a way that it does not dissociate can give no precipitate with silver nitrate.

The thermal phenomena of ionic solutions are easily explained on the basis of the Arrhenius theory. The heats of neutralization of strong acids with strong bases are all nearly equal as can be seen from Table III because the actual reaction taking place is between the hydrogen and hydroxyl ions in each case. Since the heats of neutralization are all due to the same reaction, they are necessarily equal.

TABLE III.—HEATS OF NEUTRALIZATION OF STRONG ACIDS AND STRONG BASES

Isothermal Reactions at 20°C. Data in Large Calories

Acid	KOH	NaOH	LiOH
HCl	14.014	13.895	13.993
HBr	13.989	13.840	14.010
HI	13.916	13.782	13.827
HNO_3	14.086	13.837	13.863

A practically zero heat of mixing results when two ionic solutions at the same concentration are mixed together. According to the Arrhenius theory there is no resulting thermal effect because nothing really happens, the solute molecules are in the form of ions before and after mixing. Heats of precipitation of silver chloride from various salts are all nearly equal (Table IV).

As in the case of the neutralization reactions, there is only one reaction taking place, the combination of silver ions with chloride ions to form silver chloride.

TABLE IV.—HEATS OF PRECIPITATION OF SILVER CHLORIDE FROM VARIOUS CHLORIDES

Chloride	Heat of Precipitation, Kilojoules
Na	67.8
K	67.4
NH_4	67.6
Ba	67.4
Cu	68.0
Zn	68.3
Ni	66.9
Al	67.4
Cr	68.3
H	67.6

Many years after the theory of dissociation was first advanced by Arrhenius, a direct proof of dissociation seems to have been obtained by the use of short-lived radioactive elements as indicators. Hevesy and Zechmeister* mixed a small amount of thorium B, an isotope of lead, with some lead nitrate. The presence of the minute quantity of thorium B could be detected and its quantity estimated by measuring the rate of discharge of a gold leaf electroscope, the discharge being caused by the ionization of the air due to the electrons emitted by thorium B on disintegration. The lead nitrate containing the active isotope thorium B in the form of the nitrate was mixed in solution with an equivalent amount of inactive lead chloride. When the lead chloride was recrystallized from the solution, it was found that the thorium B had distributed itself equally between the lead nitrate and the lead chloride. This exchange certainly could not have taken place if the thorium B nitrate had not dissociated in solution; for how could the thorium B have migrated from lead nitrate to lead chloride until kinetic equilibrium was reached except in the form of an ion? But no transfer of the thorium B to the lead chloride took place when the thorium B was united to carbon. Lead tetraphenyl plus the active thorium B tetraphenyl

* G. HEVESY and L. ZECHMEISTER, *Ber.*, **53**, 410 (1920); *Z. Elektrochem.*, **26**, 151 (1920). See also F. PANETH, "Radio Elements as Indicators," Chap. V, McGraw-Hill Book Company, Inc., New York, 1928.

was mixed with lead chloride in pyridine, but no migration of the thorium B took place. This proves that the interchange of atoms between molecules in solution is dependent upon the existence of an electrolytic dissociation. Tolman also proved the existence of ions by whirling solutions of electrolytes in a powerful centrifugal machine and demonstrating that a potential was set up between the two ends of the tube containing the electrolyte.

The Arrhenius theory of dissociation has been especially valuable in the fields of physiology, biology, and medicine. The great influence of the hydrogen ion upon biological reactions could never have been understood without the Arrhenius theory, nor could scientists have understood such interesting phenomena as ionic distribution, membrane equilibria, and oxidation-reduction potentials.

TABLE V

Medium	Dielectric constants	Electrolytic dissociation
Low vacuum	1.0	None at normal temperature.
Benzene	2.3	Extremely small but measurable conductivity indicates a trace of dissociation.
Ether	4.1	Noticeable conductivity of the dissolved electrolyte.
Alcohol	25	Moderately strong dissociation.
Formic acid	62	Strong dissociation of dissolved salts.
Water	80	Very strong dissociation.
Prussic acid	96	Very strong dissociation.

A question not answered by Arrhenius but one which interests us deeply is how can positively and negatively charged particles exist more or less independently in solution without coming together to form a neutral molecule? Thomson, in 1893, and Nernst, in 1894, pointed out* that dissociation was undoubtedly connected to the dielectric constant of the solvent.

Coulomb's law,

$$f = \frac{q_1 q_2}{Dr^2} \tag{12}$$

* J. J. THOMSON, *Phil. Mag.*, **36**, 313 (1893); W. NERNST, *Z. physik. Chem.*, **13**, 535 (1894).

relating the force, f, between two particles having the charges, q_1 and q_2, at the distance, r, apart states that the force of attraction or repulsion between the two particles is inversely proportional to the dielectric constant, D. (The dielectric constant is discussed in greater detail in a later chapter.) The greater the dielectric constant of the solvent the smaller will be the force of attraction between two unlike ions and the smaller, therefore, will be the tendency of the ions to form molecules. These considerations led Thomson and Nernst to state that the greater the dielectric constant of the solvent, the greater is the dissociating power of the solvent and the less are the forces tending to form molecules from the ions. In proof of this rule Nernst* quotes the facts given in Table V.

Walden† has also found that the Nernst-Thomson rule is roughly correct for the salt tetraethylammonium iodide dissolved in a variety of solvents. In this connection it is interesting to quote from a review by Audrieth and Nelson who state, "the suitability of a solvent as an ionizing medium was once believed to be dependent upon its dielectric constant. This idea has long been discarded, for it has been found that given the proper solute practically any substance may act as an ionizing medium." However, the recent important work‡ of Kraus and Fuoss proves very definitely a distinct connection between degree of dissociation and dielectric constant of the solvent. This work will be more fully considered in connection with the theory of electrical conductance of solutions. At this point the general outline of the present-day theories concerning the mechanism of dissociation will be presented.

The undissociated molecule in solution is constantly suffering collisions with the solvent molecules. The forces binding the ions together in some molecules are so weak that the solvent molecules on impact cause the solute particle to dissociate, but the forces binding other kinds of ions together may be so strong that the solute molecule can withstand the bombardment of the solvent molecules without dissociating. Of course, some solvent

* W. NERNST, "Theoretical Chemistry," 7th ed., The Macmillan Company, New York, 1916.

† WALDEN, *Z. physik Chem.*, **46**, 103 (1903); **54**, 129 (1906).

‡ C. A. KRAUS and R. M. FUOSS, *J. Am. Chem. Soc.*, **55**, 21 (1933) FUOSS and KRAUS, *ibid.*, **55**, 476, 1019 (1933).

molecules will have higher kinetic energies than others in the same solution, they will be able to give up more energy on collision and will, therefore, dissociate under favorable conditions solute particles which the greater number of solvent particles would be unable to dissociate. Such collisions, however, will be few in number. In general we can say that solute molecules whose energies of association (association is defined here as the reverse of dissociation) in a particular solvent are greater than a certain minimum value will be very little dissociated in that solvent, that molecules having a smaller binding energy will be nearly completely dissociated, and that molecules having energies in the neighborhood of the minimum value will be partially dissociated. By partial dissociation we mean that a certain fraction of the solute molecules are completely dissociated and the remaining molecules completely associated. From the above discussion it is clear that a knowledge of the energy of association is important. On the assumption of the validity of Coulomb's law, Bjerrum* calculates that the potential energy of the undissociated molecule is given by the equation

$$U = \frac{q_1 q_2}{\mathbf{a}D}, \tag{13}$$

where U is the potential energy of the ionic system when the ions are separated by the distance $\mathbf{a}$, and q_1 and q_2 the ionic charges, negative for negative ions (the discussion here is for a salt that dissociates into two ions). The distance $\mathbf{a}$ is the distance between the centers of the ions at the moment of dissociation. If D is small, $-U$ will be large so that considerable work must be done in dissociating the molecule. Kraus and Fuoss have found that Eq. (13) is substantiated by their experimental results. The salt tetraisoamylammonium nitrate is nearly completely dissociated in dioxane-water mixtures when the dielectric constant is greater than 38.0; for lower values of the dielectric constant the dissociation constant falls until it reaches the low value of 2×10^{-16} in a solution whose pure solvent, 99.4 per cent dioxane, 0.6 per cent water, has a dielectric constant of 2.38.

* N. Bjerrum, *Kgl. Danske Vidensk. Selskab*, **7**, No. 6 (1926); Falkenhagen, "Elektrolyte," pp. 257*ff.*, Leipzig, 1932. See also Fuoss and Kraus, *J. Am. Chem. Soc.*, **55**, 1021 (1933).

It is interesting to compare the energies of dissociation of the above salt per gram molecule as calculated by Fuoss and Kraus. These values are given in Table VI along with experimental values of the dielectric and dissociation constants.* In the solvents of low dielectric constant the energies of dissociation approach those of ordinary reactions, but in solvents of high dielectric constant very little energy has to be expended to dissociate the molecule.

TABLE VI

% Water	D	K	Energy required for dissociation (calories)
0.60	2.38	2×10^{-16}	21,400
1.24	2.56	1×10^{-14}	19,100
2.35	2.90	1×10^{-12}	16,400
4.01	3.48	2.5×10^{-10}	13,100
6.37	4.42	3×10^{-8}	10,300
9.50	5.84	1.65×10^{-6}	7,900
14.95	8.5	1.00×10^{-4}	5,450
20.2	11.9	9.0×10^{-4}	4,150
53.0	38.0	0.25	820

The extent of dissociation of the solute molecules also depends, according to Bjerrum's theory, on the size of ions as is evident from Eq. (13). Molecules formed of large ions will have small energies of dissociation and will, therefore, be easily ionized by collisions with the solvent molecules. Conversely molecules formed of small ions will be little dissociated even in solvents having a high dielectric constant. Fuoss and Kraus point out that silver nitrate is more completely dissociated in ammonia, dielectric constant of 22, than in benzonitrile, dielectric constant

* The dissociation energies, ΔG°, are the free energies of the reaction

$$AB \rightarrow A^+ + B^-$$

(the products and reactants being in their standard states) and are obtained from the experimental values of the dissociation constant by means of the equation $\Delta G^\circ = -RT \ln K$. This equation is derived in the chapter on Thermodynamics.

25.2, because the silver ion is relatively large in ammonia due not only to the formation to the stable ammonia complex ion, but also to solvation. Thus we see that ion size is an important factor in dissociation.

We may now answer our original question as to the cause of dissociation. Molecules or ions existing on the surface of crystals in contact with a solvent will break away from the solid due to their thermal motion. In the solution the molecules will be dissociated by either high- or low-speed impacts with the solvent molecules depending upon the energies involved. The ions when dissociated will combine with or become solvated to the solvent molecules so as to increase their effective size. This increase in size will diminish the energy of association as will also the increase in the dielectric constant of the medium between the ions when the ions become separated by the solvent molecules. The energy of association may decline to so low a value that the ions are unable to exist as neutral molecules in solution in which case the solute will be practically completely dissociated. Another way of looking at dissociation is to imagine the ions combining with the solvent, giving out heat of solvation, and sinking to such low potential energy levels that a stable situation is produced.

A word should be said concerning the meaning of the terms "dissociation" and "ionization." Dissociation may be defined as the separation or splitting up of a molecule into two or more parts and does not necessarily mean the formation of ions. Thus gaseous ammonium chloride dissociates into the neutral entities, ammonia and hydrogen chloride. Ionization, on the other hand, is to be thought of as the formation of ions, and since this may occur within a molecule by the transfer of electrons, ionization does not necessarily imply dissociation. Cesium fluoride molecules in the gaseous condition may be conceived of as being completely ionized, even though they are not dissociated. The process of electrolytic dissociation or ionization is probably a combination of both phenomena. When a sodium chloride molecule dissociates into two ions, the electron becomes completely removed from the sodium and passes over to the chlorine atom so that ionization also occurs. There is no direct evidence

for believing that the valence electron of the sodium is completely removed from the sodium atom in solid sodium chloride.

In concluding this chapter which finishes the general introduction to the subject of electrochemistry the author wishes once again to emphasize the importance of the electrolytic dissociation theory. In 1887 Arrhenius laid one of the foundation stones upon which the structure of electrochemistry has been built.

CHAPTER III

ELECTROLYSIS

Units.—The ultimate unit of negative electricity is called the **electron,** and may be considered as being a discrete particle, recently discovered to have wave properties. The mass of the electron cannot be determined experimentally independently of its charge, but if we assume that the electron has a definite and constant quantity of electricity associated with it, we can then say that its mass is equal to 8.99×10^{-28} g. when its velocity is zero and equal to infinity when it is moving with the speed of light. Conversely we might also say that its mass is constant and that its charge is equal to 4.77×10^{-10} e.s.u. (electrostatic units) at zero velocity and equal to zero when the electron has the velocity of light, but, according to the theory of relativity, the first assumption is to be preferred. Millikan measured accurately the quantities of electricity that a minute oil drop could take on and he found these amounts always to be equal to, or a multiple of, 4.77×10^{-10} e.s.u.; hence this figure represents the "atom of electricity."

There are several units of positive electricity,* the **positron,** the **proton,** and the **deuteron.** The mass of the positron is practically equal to that of the electron, the mass of the proton is nearly equal to the mass of the hydrogen atom, and the mass of the deuteron is approximately twice that of the proton. The quantity of positive electricity associated with the proton is equal and opposite to that of the electron, *viz.*, 4.774×10^{-10} e.s.u. if the electron is -4.774×10^{-10} e.s.u.

The motion of electricity through space gives rise to an electrical current, the magnitude of the current depending upon the number of moving electrical particles and upon their velocity. The sign of the electrical current may be considered as negative if electrons are flowing in one direction or positive if protons are flowing in the same direction. Conversely a change of direction

* C. D. ANDERSON, *Phys. Rev.*, **43**, 491 (1933).

of either the electrons or the protons changes the sign of the current. The simultaneous passage of both positive and negative particles in a conductor also gives rise to a current since positive particles flow in an opposite direction to negative particles, and the flow of positive electricity in one direction has the same sign as the flow of negative electricity in the other; in other words the electrical effect of the motion of the two types of particles is additive. In electrolytic solutions the current is due to the motion of both positive and negative electricity, but in metallic conduction it is generally due solely to the flow of the electron.*

If, in a conductor, 6.28×10^{18} electrons flow through a certain cross section in one second, the current is equal to one **ampere.**†

In defining the units of current, voltage, and resistance it must be remembered that there are four systems, the electrostatic, the electromagnetic, the practical absolute, and the international. The electrostatic system is the system used most in theoretical calculations while the international system, which differs from the practical absolute by only a very small factor, is the basis of nearly all experimental work. The **international ampere** is defined‡ as the "unvarying electric current which, when passed through a solution of nitrate of silver in water, in accordance with the [attached] specifications . . . , deposits silver at the rate of 0.00111800 of a gram per second." Most recent work indicates that the absolute ampere and the international ampere are practically identical. It is predicted that in a few years the absolute system will replace the international system necessitating thereby a change in the value of the customarily used volt and ohm.§

* The motion of protons in platinum has been discovered by Coehn: A. Coehn and W. Specht, *Z. Physik*, **62**, 1 (1930); *Science Abstracts*, **33A**, 936 (1930). See also D. P. Smith and F. H. Martin, *J. Am. Chem. Soc.*, **38**, 2577 (1916); E. A. Harding and D. P. Smith., *ibid.* **40**, 1508 (1918); D. P. Smith, *Proc. Nat. Acad.*, **7**, 28 (1921); *Z. Physik*, **69**, 253 (1931).

† The ampere is named in honor of the French physicist, A. M. Ampère (1775–1836), who discovered an important law connecting the strength of an electric current with the force exerted upon its conductor by a known magnetic field.

‡ *Bur. Standards Circ.*, 29, Washington, 1910.

§ For a discussion of the units of electrical measurement see G. W. Vinal, *Trans. Electrochem. Soc.*, **55**, 43 (1929).

The **international coulomb*** is defined as the amount of electricity conveyed in one second by a current of one international ampere. The total number of coulombs is equal to the number of amperes times the total number of seconds that the constant current has flowed through the conductor.

The motion of electrons in a conductor is not frictionless except, possibly, in the neighborhood of the absolute zero. Therefore in order to move the electrons through the conductor at a constant velocity, a constant accelerating force must be applied to them. This force originates in the electrical potential difference between the two ends of the conductor. Let us designate **electric potential** by ψ and **electric potential difference** (commonly measured in volts) by E.

E signifies difference in potential whether due to a potential drop along a conductor or to an electromotive force existing at some boundary. $\mathbf{E}$ signifies electric field strength or component of the electric field along some direction, and may be taken as a vector quantity. When $\mathbf{E}$ and other **bold-faced** symbols are to be treated as vectors, due notice will be given, but usually $\mathbf{E}$ will refer solely to the scalar magnitude of the field strength.

Imagine a conductor 8 cm. long composed of two kinds of wire of the same size such that the voltage difference between the 2 cm. A to B (Fig. 1) is 4 v. and that between the remaining 6 cm., B to C, is 2 v. The electrical force on an electron in the conductor between A and B is greater than between B and C since the potential fall is greater over a smaller distance. The force is mathematically equal to the negative of the slope of the lines in the plot, or (for a unit charge)

* The coulomb was named for the French physicist C. A. Coulomb (1736–1806), who discovered the fundamental inverse square law of electrical attraction. There are ten practical coulombs in one electromagnetic unit. and 3×10^{10} electrostatic units of charge in one electromagnetic unit. It is perhaps interesting to point out here that Maxwell's differential equation for the X-component of an electric field as a function of x, y, z, and time gives as the velocity of electromagnetic "disturbance" or wave the value 3×10^{10} cm. per second which as stated above is the number of electrostatic units of charge in an electromagnetic unit. On the basis of his equations Maxwell postulated in 1865 that light was an electromagnetic phenomenon, and in agreement with his theoretical result both the velocity of light and the velocity of electromagnetic waves were found experimentally to be equal to 3×10^{10} cm. per second.

$$\text{Force} = \frac{-d\psi}{dx} = X,$$

where X is the component of the electric field strength ($\mathbf{E}$) in the x-direction. Thus the accelerating force, *i.e.*, the electric field strength, between AB is numerically equal to $4/2$ and between BC to $2/6$ v. per centimeter. It is important to distinguish between voltage, E, and the electric force or electric field-strength, $\mathbf{E}$ (or its x-component, X) which is volts per centimeter.

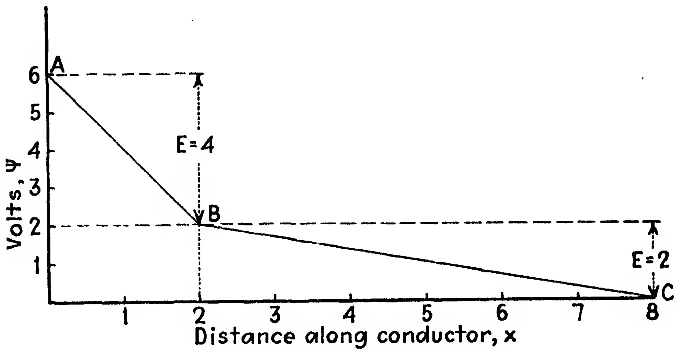

Fig. 1.

The unit of electrical resistance is the **ohm** and is defined by international agreement as "the resistance offered to an unvarying electric current by a column of mercury at the temperature of melting ice, 14.4521 grams in mass, of a constant cross-sectional area, and of a length of 106.300 centimeters." If this definition had stipulated a length of about 106.245 cm., the absolute and international ohm would have been exactly the same.

The international ampere and ohm are the standards; the **international volt,** defined in terms of international amperes and ohms, is the difference of potential "which, when steadily applied to a conductor whose resistance is one international ohm, will produce a current of one international ampere." This definition was suggested by the important relationship discovered by Ohm in 1827, *viz.*,

$$I = \frac{E}{R}, \tag{1}$$

where I is the current, R is the resistance of the circuit, and E is the difference in voltage between the two ends of the circuit.*

As an electron or any charged particle flows through a conductor, the work necessary to overcome the frictional retarding force is transformed into heat energy; the unit of this energy is called the **joule** (J) for the Englishman, J. P. Joule (1818–1889), who first determined the mechanical equivalent of heat. Joules are equal to the voltage multiplied by the total number of coulombs passed through the conductor; 4.182 joules equal one 15.5° caloric (the heat necessary to raise one gram of water from 15 to 16°C.). If τ is time in seconds, the heat produced in a conductor is given by the following equation:

$$EI\tau = J, \tag{5a}$$

or

$$I^2R\tau = J. \tag{5b}$$

* Ohm's law may also be stated in vector notation by saying that the vector of current density (current density is amperes per square centimeter of cross section of the conductor), **i**, is proportional to the electric field strength, the proportionality constant, κ is called the specific conductance. The mathematical relation is

$$\mathbf{i} = \kappa\mathbf{E}. \tag{2}$$

Multiplying this equation by Ads, where A is the cross-sectional area of the conductor and ds is the length of an element, we obtain

$$Ids = \kappa A\mathbf{E}ds \tag{2a}$$

since

$$\mathbf{i} = \frac{I}{A}\frac{\mathbf{ds}}{ds}.$$

Multiplying again by the unit vector $\mathbf{ds}/ds$, Eq. (2a) becomes

$$Ids = \kappa A\mathbf{E}\mathbf{ds}$$

since

$$(\mathbf{ds})^2 = (ds)^2. \tag{3}$$

The integral of ds is l, the length of the conductor, and of $\mathbf{E}\mathbf{ds}$ is E; hence

$$I = \frac{\kappa A}{l}E. \tag{4}$$

The resistance, R, must be equal to l/AK and is, therefore, proportional to the length of the conductor and inversely proportional to the area of cross section. We shall have occasion to consider this relationship again in measuring the electrical conductance of solutions. Ohm's law is valid only as long as κ is constant; it must be remembered that for certain conductors κ may be a function of temperature, exposure to light, magnetic fields or very high potentials.

The above equations are based on the tacit assumption that Ohm's law is valid, *i.e.*, that all the electrical energy is turned into heat energy. There must be no electrical work done by the system.

Series and Parallel Circuits.—It is possible to connect together a number of conductors in more than one way. The simplest system is the *series* arrangement in which the conductors are all connected end to end as in Fig. 2. The current passing through the various segments is necessarily the same; the total resistance

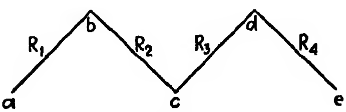

Fig. 2.

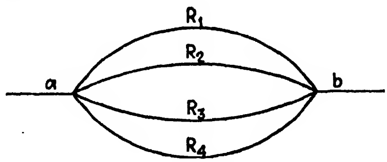

Fig. 3.

of the system is the sum of the separate resistances of the conductors,

$$R = R_1 + R_2 + R_3 + R_4. \tag{6}$$

Similarly, the total voltage drop is equal to the sum of the separate voltage drops, *viz.*

$$E_{ae} = E_{ab} + E_{bc} + E_{cd} + E_{de}. \tag{7}$$

If the conductors are connected so that their two ends all meet at two points as in Fig. 3, the relationships are different. The total current, I, is the sum of the separate currents

$$I_{ab} = I_1 + I_2 + I_3 + I_4. \tag{8}$$

Applying Ohm's law to Eq. (8), we get

$$\frac{E_{ab}}{R} = \frac{E_{ab}}{R_1} + \frac{E_{ab}}{R_2} + \frac{E_{ab}}{R_3} + \frac{E_{ab}}{R_4}.$$

The potential drop across the branches is the same for all, hence

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3} + \frac{1}{R_4}. \tag{9}$$

Figure 3 represents several conductors connected in *parallel.*

Conductors have sometimes been classified as conductors of the *first class* in which no ponderable matter moves, and of the *second*

class, in which matter is transported as the current flows. This distinction seems to be breaking down with the realization that the electron has mass and with the knowledge that protons, for example, can carry the current to some extent in metals.

The Electrolysis of Simple Substances and Faraday's Laws. Before the end of the eighteenth century Paets van Troostwijk and Deimann had succeeded in decomposing water electrically.* The possibility of accomplishing this rests in the fact that electrons do not migrate through aqueous solutions under the force of an external potential, but *ions* do. Let us first consider the case of two electrodes of great chemical inertness, such as electrodes made of platinum, dipping into a dilute sulfuric acid solution (Fig. 4), and let a potential be applied to the electrodes such that positive electricity flows from left to right through the solution. This means that electrons will flow through the metallic conductors to the right; but when the electron reaches the surface of the platinum, since it cannot migrate through the solution, it will combine with the hydrogen ion, which is positive in the solution, and hydrogen gas will result. At the other electrode, the negative hydroxyl ion will give up its excess electron to the platinum, oxygen will come off according to the reaction

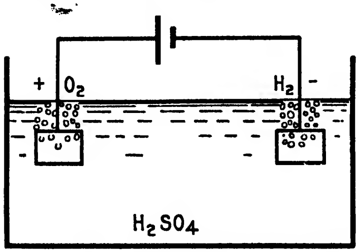

FIG. 4.

$$2OH^- \rightarrow O_2 + 2H^+ + 4\epsilon^-,$$

and the electrical current will have passed through the cell.

Faraday, who discovered the quantitative relations underlying electrolysis, gave to the two types of electrodes and ions the names they bear today. Since he had no particular basis for

* *Observations sur la physique*, **35**, 369 (1789). The electrical decomposition of water has always held a great popular fascination. The author vividly remembers, while a student, hearing an oration given by a famous politician in which the speaker declared that were it possible to develop a large-scale method for the decomposition of water (which could now be accomplished in the laboratory), the ocean would provide us with an inexhaustible supply of fuel since water contains the gases hydrogen and oxygen which when burned together give off a considerable amount of heat. It is left to the student to discover the fallaciousness of the great orator's argument.

naming the electrodes, he called the one toward the east in his apparatus the **anode,** which was the positive electrode, and the one toward the west the **cathode,** which was the negative electrode. The bodies which migrated through the solution he called ions (from the Greek meaning wanderer); those that migrated to the anode he called **anions** and those that migrated to the cathode, **cations.** Since the anode is the positive electrode, the anions that it attracts must be the negative ions; similarly the ions that are attracted by the cathode, the negative electrode, are the cations or positive ions. This is a rather confusing nomenclature, but after long usage the student will become quite familiar with it.

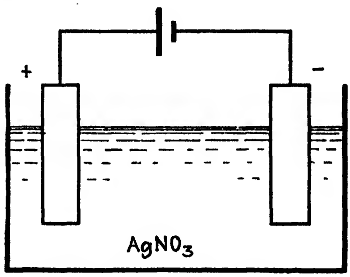

Fig. 5.

It is interesting to observe the electrolysis of a solution when the electrodes are no longer inert but are active electrodes such as silver electrodes in a silver nitrate solution. When the current passes through the cell (Fig. 5) as before, electrons at the right-hand electrode, the cathode, combine with the positive silver ion, the cation, to form metallic silver on the surface of the electrode. Hence the cathode will gain in weight. At the anode, metallic silver atoms will give up an electron which will then flow to the right through the silver wire, and the silver will go into solution as a positive ion, or cation. Hence the anode will lose in weight.

Other electrode reactions in addition to deposition or solution of a gas or metal are the increase in valence of an anion or a cation such as the conversion of Fe^{++} to Fe^{+++} at the anode and the conversion of $Fe(CN)_6^{---}$ to $Fe(CN)_6^{----}$ at the cathode, the formation of complex anions at the anode or complex cations at the cathode and the formation of insoluble substances such as silver chloride on a silver anode or lead dioxide on a lead anode.

Faraday was the first to measure these chemical effects of the electric current quantitatively and he discovered the laws of electrolysis that bear his name.* The first law of electrolysis as

* See "The Fundamental Laws of Electrolytic Conduction." Memoirs by Faraday, Hittorf, and F. Kohlrausch. Edited by H. M. Goodwin, Harper & Brothers, New York, 1899.

stated by Faraday is "the chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes," and the second law "several substances were placed in succession, and decomposed simultaneously by the same electric current. . . . It is needless to say that the results were comparable, the tin, lead, chlorine, oxygen, and hydrogen evolved being *definite in quantity* and electrochemical equivalents to each other." In modern phraseology we should describe Faraday's laws by the single statement, *the number of equivalents of any substance liberated or deposited at an electrode is exactly proportional to the quantity of electricity which passes across the metal-solution junction.* Faraday found that his laws were true irrespective of the shape of the electrode, of the temperature, of the rate with which the electricity was passed, and that it was also true irrespective of the nature of the solution (called the electrolyte) in the cell.

Faraday's laws are among the most exact of nature, and these are important not only for electrochemical reactions but because they gave the first insight into the electrical nature of matter and into the atomicity of electricity. Faraday himself wrote:* "I think I cannot deceive myself in considering the doctrine of definite electrochemical action as of the utmost importance. It touches by its facts more directly and closely than any former fact, or set of facts, have done, upon the beautiful idea, that ordinary chemical affinity is a mere consequence of the electrical attractions of the particles of different kinds of matter; and it will probably lead us to the means by which we may enlighten that which is at present so obscure, and either fully demonstrate the truth of the idea or develop that which ought to replace it."

The Faraday and the Coulometer.—It is evident that if the same quantity of electricity deposits chemically equivalent weights of substances on the electrodes, there must be a definite quantity of electricity which will liberate one gram-equivalent of any element. This quantity is called the faraday in honor of Faraday, is denoted by F, and has been found by experiment to be equal to 96,494 ± 5 coulombs. The experimental procedure necessary to determine this figure consists in running a carefully measured current for a known duration of time through an

* *Phil. Trans.*, **124**, 77 (1834).

electrolytic silver nitrate cell. The silver deposited is weighed, and the value of the faraday is calculated.

The accurate knowledge of the faraday is very important for several reasons. In combination with Millikan's value for the electric charge on a single electron it is possible to calculate the number of electrons necessary to give one faraday, and this in turn gives the number of atoms per gram-equivalent, or Avogadro's number. Since the electron is equal to 1.591×10^{-19} coulomb, the number of atoms per gram-equivalent of a

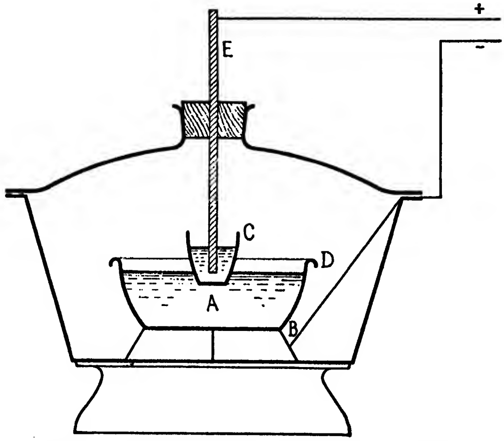

FIG. 6.—The Richards porous-cup coulometer.

univalent element is $96{,}495/1.591 \times 10^{-19}$ or 6.064×10^{23}. A knowledge of the faraday also enables us to calculate the total number of coulombs passed through a system by means of an instrument called by T. W. Richards the *coulometer*. This is of great practical advantage, for frequently it is necessary to know with precision the total number of coulombs under conditions of varying current when it would be well-nigh impossible to calculate the coulombs accurately by multiplying the amperage by the time.

There are many types of coulometers; of these the most accurate type, the Richards porous cup coulometer will be described first (Fig. 6). It consists of a platinum crucible or dish, *A*, which serves as the cathode. Electrical connection to the cathode is made through the brass ring *B* on which the cathode rests. The porous alundum cup *C* is held in place by a

little glass triangle *D* and dips down into the 10 per cent silver nitrate solution which is contained in the platinum dish. The anode *E* is a thick silver rod whose end is dipped into the silver nitrate solution inside the porous cup. The purpose of the porous cup is to collect the anode mud, fine particles of silver, that drop off the silver anode as the electrolysis proceeds. This silver mud should not, of course, be weighed with the electrolytic silver that deposits on the cathode. The whole apparatus is conveniently contained in a desiccator (without any drying agents) to keep

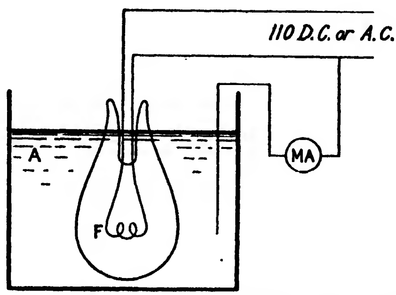

FIG. 7.—The sodium electric-light-bulb coulometer.

dust from falling into the platinum dish. The platinum dish is weighed before and after the passage of the current, the increase in weight being the weight of silver deposited. This value divided by the atomic weight of silver and multiplied by the faraday gives the number of coulombs passed through the apparatus. Rosa and Vinal* have made an accurate study of the silver coulometer and give detailed directions for its operation.

In recent times a sodium coulometer has been made by inserting an electric light bulb into molten sodium nitrate and running the current in such a direction that sodium ions migrate into and through the glass until they reach the inside surface of the bulb where they deposit out as metallic sodium in the form of a brilliant metallic film.† The mechanism of this coulometer is made clear by reference to Fig. 7. Alternating current of 110 v. heats the filament *F* to incandescence so that thermionic electrons stream away from the filament toward the walls of the glass bulb. At the inside bulb surface these electrons meet the entering

* ROSA and VINAL, *Bur. Standards, Sci. Papers*, 285 (1916).
† R. C. BURT, *J. Opt. Soc. Am.*, **11**, 87 (1925); *Phys. Rev.*, **27**, 813 (1926).

sodium ions and combine with them forming metallic sodium. The increase in weight of the bulb gives the weight of sodium deposited. The potential difference between F and A, the fused sodium nitrate, necessary to bring about the electrolysis may be obtained from either an alternating or a direct current inasmuch as the bulb acts as a rectifier; *i.e.*, owing to the fact that the thermionic electrons can only stream in one direction, the sodium ions can only go through the bulb in one direction.

Stewart,* in a carefully performed research, has shown that the error of the sodium coulometer may be reduced to less than one part in ten thousand by making a bulb out of a highly conducting glass (see Fig. 8) and running the current in such a direction that the sodium ions leave the glass instead of enter it. A platinum wire is sealed through the glass and dips into cadmium in which there is some metallic sodium. The whole tube is placed in the molten sodium nitrate and the electrolysis then carried out. The loss in weight of the coulometer gives the equivalents of sodium liberated.

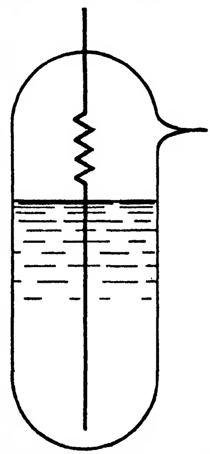

FIG. 8.—Stewart's sodium coulometer.

Coulombs may be measured in a number of other ways, for example, by weighing the copper deposited from a copper sulfate solution, by measuring the volume of mixed hydrogen and oxygen evolved from platinum electrodes in sulfuric acid or from nickel electrodes in fairly concentrated hydroxide solutions, by titrating the iodine deposited on platinum anodes, or by titrating silver ions electrically dissolved into potassium nitrate solutions. Washburn and Bates† have shown that the error of the iodine coulometer is less than 0.002 per cent.

The Wright‡ coulometer, illustrated in Fig. 9, enables a rather rough measure of coulombs to be made with surprising ease.

* O. J. STEWART, *J. Am. Chem. Soc.*, **53**, 3366 (1931).

† WASHBURN and BATES, *J. Am. Chem. Soc.*, **34**, 134 (1912).

‡ See HATFIELD, *Z. Elektrochem.*, **15**, 728 (1909); SCHULTE, *ibid.*, **27**, 475 (1921); CREIGHTON, "Principles of Electrochemistry," p. 22, John Wiley & Sons, New York, 1924.

The modification illustrated in Fig. 9 is due to Evans and Field of the Northwestern Chemical Laboratory.

The apparatus is filled with a solution of potassium mercuric iodide (225 g. HgI_2 and 750 g. of KI per liter), and mercury is poured into the annular depression *A* through the opening *B*. The cathode is the carbon rod *C*, the anode being the mercury in the circular channel. As the current flows, mercury goes into solution at *A* and after a certain time lag (which must be corrected for, or eliminated, by measuring the mercury deposited between two later moments) mercury will deposit on *C* and drip off through the solution into the measuring tube *D*. The height of the mercury in *D* can be calibrated in terms of ampere-hours. When the tube *D* has filled up, the mercury can be run out through the stop cock *E* and returned to the anode through *B*. There is no loss of material in this coulometer and no evolution of gases; iodine may deposit at *A*, but it will slowly react with mercury regenerating the mercuric iodide. This coulometer which may be made of cast iron has many commercial applications.

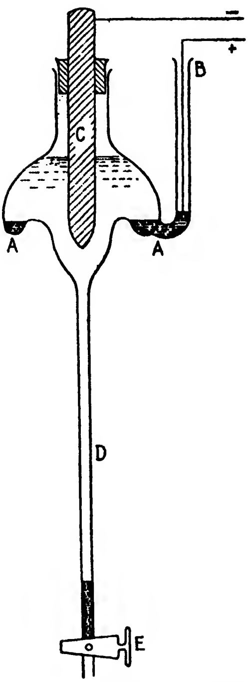

FIG. 9.—The Wright coulometer.

Current Density, Current Efficiency, and Other Factors Involved in the Deposition of Elements.—There are many instances of apparent failure of Faraday's laws; for example, if the concentration of silver nitrate in the solution of the silver coulometer becomes too low or if the amperage becomes too high, silver may not be deposited quantitatively in accordance with Faraday's laws, but side reactions such as the evolution of gas may interfere. One of the most important factors governing the proper deposition of elements is the *current density*, which is defined as the amperes per square centimeter of available electrode surface. Thus, if the amperage is 1.62 and the cathode has a total surface of 4 sq. cm., the current density for the cathode is 0.405. At the same time if the anode has a total surface of 3 sq. cm., the current density for the anode is 0.54. The maximum current density permitted for the proper deposi-

tion of any element up to the present time has been found only after an experimental study of the factors involved. It is known that a rapid rotation of the electrolyte or electrodes permits a higher current density, as does a higher concentration of the dissolved salt. The presence of small amounts of addition agents such as peptone, or glue in the case of lead, helps to obtain a coherent deposit. The temperature must be properly controlled, and in general the acid concentration of the solution is important. Many metals cannot be deposited from aqueous solutions, and in this case recourse must be had to nonaqueous solutions, such as liquid ammonia.* The proper current densities for deposition from liquid ammonia seem to be lower than for the deposition of the corresponding metals from water solution.

The actual yield of element or compound obtained divided by the amount theoretically calculated by Faraday's second law times 100 gives the *current efficiency* or the percentage yield of the process. In the silver coulometer this may be considered to be equal to 100 per cent, but in the electric-light-bulb type it is slightly less than 100 per cent owing to the tendency of silicate ions to be electrolyzed out of the glass instead of sodium ions into it. The current efficiency of most industrial processes is generally less than 100 per cent and may fall as low as 66 per cent or even lower. The deposition of foreign elements, evolution of extraneous gases, mechanical loss, vaporization of the deposit at high temperature, side reactions of the deposit with the electrolyte or its solution in the liquid, and leakage of current may all contribute to the reduction of the current efficiency of the process.

Another factor of considerable industrial importance is the *energy efficiency* of the process. Electrical energy is volts times coulombs, or joules; the theoretical minimum energy necessary for the deposition of an element being equal to the reversible voltage (this will be considered in more detail later) times the theoretical quantity of electricity needed to complete the process. However, in all actual industrial procedures, voltage in excess of the theoretical must be used in order to overcome internal resistance of the electrolyte, and any potentials operating in opposition to the applied potential. We can say, then, that

* L. F. Audrieth and H. W. Nelson, *Chem. Rev.*, **8**, 335 (1931).

the voltage efficiency times the current efficiency is the energy efficiency or

$$\text{Energy efficiency} = \frac{\text{theoretical voltage}}{\text{actual voltage}} \times \frac{\text{theoretical quantity of electricity}}{\text{actual quantity of electricity}} \times 100.$$

Since electricity is sold on the basis of electrical energy rather than on the basis of quantity of electricity, it is evident that energy efficiency is more important industrially than current efficiency.

It should also be emphasized that the passage of large currents through an electrolyte often produces considerable heating effects depending upon the internal resistance of the system, the magnitude of the heat energy produced being equal to I^2Rt expressed in joules. In the commercial electrochemical production of aluminum, the heating effect of the current is sufficient to keep the electrolyte in a molten condition; aluminum is reduced at the carbon cathode, separates from the cryolite aluminum oxide bath, and can be tapped off.

Exercises

1. *a.* The platinum cathode of a silver coulometer increased 0.2105 g. in weight during an electrolysis. How many equivalents of silver were deposited? How many coulombs of electricity passed?

b. If the above electrolysis lasted 16 hr., what was the average current?

2. A current of 0.1 amp. passes simultaneously through solutions of hydrochloric, sulfuric, and phosphoric acid for 3 hr. Calculate the weight of hydrogen liberated in each case.

3. If the volumes of 1 mole of hydrogen and oxygen gas under standard conditions are 22.43 and 22.39 l., respectively, what would be the total volume of gas liberated under standard conditions from platinum electrodes immersed in dilute sulfuric acid if a current of 0.002 amp. was passed for 10 min.?

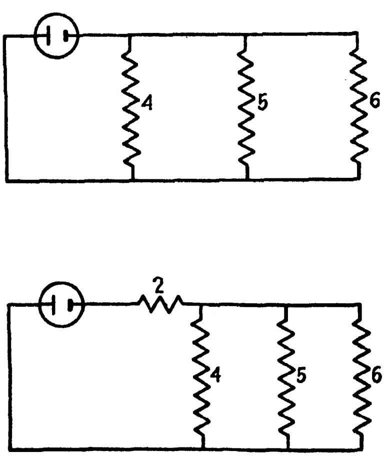

Fig. 10.

4. Ten amperes in 10 hr. liberate how much aluminum from a cryolite aluminum oxide bath?

5. Calculate the current in each of the branches of the circuits of Fig. 10 and total current through the cell. Numbers assigned to the resistances give the resistance of each in ohms. The e.m.f. of the cell is 3 v. in each case. Assume that the cells have zero internal resistance.

6. How many calories are given off by a resistance of 10 ohms if a current of 0.1 amp. is passed for 25 min.?

7. An electric heater which runs on 110 v. direct-current heats 25 l. of water 5°C. in half an hour. What is the resistance of the heater?

8. List the products of electrolysis at each electrode of the following cells:

a. A carbon anode and iron cathode in a dilute solution of potassium chloride. The same in a concentrated solution of hydrochloric acid.

b. A nickel anode and cathode in a concentrated solution of sodium hydroxide.

c. A sodium amalgam anode and a silver chloride cathode in a solution of sodium chloride.

d. A platinum anode and cathode in a concentrated nitric acid solution.

9. Write chemical reactions for the changes taking place in the above cells during the electrolysis.

CHAPTER IV

THE MEASUREMENT OF THE ELECTRICAL CONDUCTANCE OF SOLUTIONS

Units.—In the last chapter we were concerned chiefly with the reactions at the electrode when an electric current was passed into and out of a solution through two metallic conductors. It next becomes of interest to inquire into the mechanism of electrical conductance in the body of the solution, but before the interesting theoretical development of this subject is taken up, let us consider actual experimental methods (which are independent of any solution theories) for measuring the conductance of electrolytes.

In the derivation of Ohm's law in the last chapter, it was found that the total resistance of a circuit was given by the equation

$$R = \frac{1}{\kappa}\frac{l}{A}, \tag{1}$$

where R is the resistance, κ the **specific conductance,** l the length of the conductor, and A the area of its cross section. Since Ohm's law is equally valid for electrolytic solutions, as Jones and Bollinger* have recently reconfirmed, we may apply Eq. (1) to electrolytic solutions.

Let us consider an electrolytic cell† 1 sq. cm. in cross section and 1 cm. long so that

$$R = \frac{1}{\kappa}. \tag{2}$$

From Ohm's law $I = E/R$. Hence κ becomes numerically equal to the current I, when E, the potential fall, is equal to unity,

* Grinnell Jones and G. M. Bollinger, *J. Am. Chem. Soc.*, **53**, 1207 (1931).

† An electrolytic cell is any apparatus that contains two electrodes immersed in or in contact with an electrolyte.

$$I = \frac{E}{R} = \frac{1}{R} = \kappa. \tag{3}$$

κ has the dimensions of ohm^{-1} cm.$^{-1}$

Although κ is the quantity that is measured in any actual experiment, it is interesting to find the conductance due to a mole of dissolved electrolyte. If the hypothetical cell 1 sq. cm. in cross section and 1 cm. long assumed in the derivation of Eq. (2) contains exactly one mole, the specific conductance is equal to the molal conductance, but as one mole of electrolyte is never dissolved in 1 cc. of solution, the specific conductance will always be less than the molal conductance. Imagine two plates 1 cm. apart and of such magnitude in area that the solution between them is of sufficient volume to hold one mole, then the reciprocal of the resistance between the two plates, or the conductance, is equal to the **molal conductance** $\bar{\Lambda}$. Similarly, if the volume of solution between the two plates contains exactly one equivalent, the conductance between the plates is equal to the **equivalent conductance,** Λ. A one molal (or molar) solution contains one mole dissolved in 1,000 cc. of solution; hence in this case $\bar{\Lambda}$ equals 1,000 times the specific conductance. A one-tenth molal solution contains one mole dissolved in 10,000 cc. of solution and the molal conductance equals 10,000 times the specific conductance, or in general

$$\bar{\Lambda} = \frac{1{,}000}{c}\kappa, \tag{4}$$

where c is the concentration of the electrolyte in moles per liter of solution. Similarly

$$\Lambda = \frac{1{,}000}{N}\kappa, \tag{5}$$

where N is the number of equivalents per liter of solution (the normality). The equivalent or molal conductance has the dimensions ohms^{-1} cm.^{2}.*

* Concentrations are frequently expressed in moles per 1,000 grams of water (designated by the symbol m) rather than in moles per liter of solution (designated by the symbol c), since this method gives values that are independent of temperature. But practically all the theoretical treatment requires the concentrations to be expressed in moles per liter of solution; hence this terminology will be chiefly used in this book.

The Direct-current Wheatstone Bridge.—Of the many different methods for the measurement of the electrical conductance of solutions, only the alternating-current Wheatstone bridge method will be described in detail here. This technique was first invented by Kohlrausch* over 30 years ago, a pioneer whose accurate and painstaking work even today excites the admiration of electrochemists.

Since Kohlrausch's fundamental inventions, the development of electrolytic conductance methods has been carried forward chiefly by Americans among whom may be mentioned Noyes, Washburn, Kraus, Cady, Parker, Hall, Adams, Shedlovsky, and finally Jones and his Harvard coworkers.

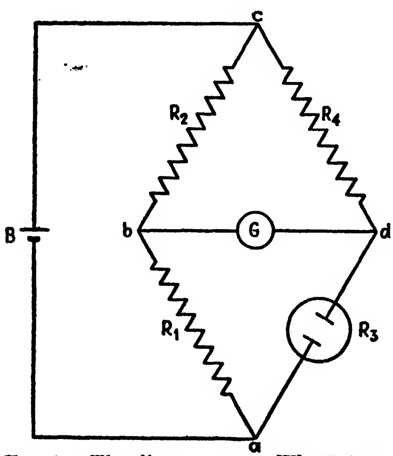

FIG. 1.—The direct-current Wheatstone bridge.

The Wheatstone bridge was invented by Christie of England and has the following form for direct current (the direct-current bridge will be considered first as its theory is somewhat simpler than the alternating-current bridge): The direct current to operate the bridge (Fig. 1) is supplied by the battery, B, which gives a potential drop, E, between the terminals a and c. R_1, R_2, and R_4 are known resistances; R_3 is the unknown resistance to be measured and G is a galvanometer to detect the flow of current between the points b and d. The technique of manipulation is to vary the known resistance R_4 until no current flows through the galvanometer. When this condition is attained, b and d must be at the same potential; hence

$$E_{ab} = E_{ad}$$

and

$$E_{bc} = E_{cd}. \tag{6}$$

* F. KOHLRAUSCH and L. HOLBORN, "Leitvermögen der Elektrolyte," Teubner, Leipzig.

Introducing the value of E given by Ohm's law into Eq. (6), we get

$$I_{ab}R_1 = I_{ad}R_3$$

and

$$I_{bc}R_2 = I_{dc}R_4. \tag{7}$$

But

$$I_{ab} = I_{bc}$$

and

$$I_{ad} = I_{cd}.$$

Hence

$$\frac{R_1}{R_2} = \frac{R_3}{R_4}, \tag{8}$$

and if R_1 equals R_2 as is generally the case,

$$R_3 = R_4.$$

Only very indirectly, however, is it possible to measure electrolytic conductances by the direct current because as the direct current flows through the cell, electrolysis occurs, changing the concentration of the solution and the nature of the electrode. These effects would result in a change in the electrical resistance of the cell and an erroneous, irregular, and varying measurement would be obtained. These difficulties are largely eliminated by the application of alternating current. In this case the electrolysis is inappreciable since the direction of the current changes 2,000 to 4,000 times a second. Unfortunately, the use of alternating current increases the difficulties of measuring the resistance electrically, but with proper precautions all apparent sources of error may be reduced to a negligible quantity.

The Theory of Alternating Currents.—Ohm's law as expressed by Eq. (3) is not valid for alternating currents inasmuch as a rapidly increasing and diminishing current sets up or produces about the conductor a rapidly increasing and diminishing magnetic field which, cutting the conductor, tends to induce in the conductor an opposing alternating current. This effect, called induction, has the result of increasing the apparent resistance or more accurately of increasing the **impedance** of the circuit (but not the true resistance), the extent of the increase being a function of the frequency. The greater the frequency, or the greater the change of current with time, the greater is the rate

of change of the magnetic flux in the conductor and the greater, therefore, is the induced opposing electromotive force. The inductive power of a circuit, or the **inductance,** is measured in units of **henries,** one henry being the inductance of a circuit in which an increase in current strength at the rate of one ampere per second produces a back electromotive force of one volt. Inductance may be compared to inertia while electrical resistance may be compared to mechanical friction. Friction and resistance continually oppose the motion of a body or of electricity, while inertia and inductance only oppose a change in the motion of a body or a change in the magnitude of a current. Inertia does not oppose the motion of a body moving with constant velocity, nor does inductance have any effect upon constant direct currents.

The simple Ohm's law is also not valid for a circuit which includes a **capacitance.** A capacitance may be considered to be a conductor having nearly an infinite direct-current resistance such as two electrodes separated by an air gap or by some other insulating material (the dielectric) such as glass, bakelite, etc. If an electromotive force is applied to the two ends of the capacitance or **condenser,** as the electrode-dielectric system is called, a momentary flow of current takes place which soon ceases. The flow of current is due to a so-called "displacement" current in the dielectric and falls immediately to zero because the backward force of the electric stress in the dielectric which is set up by the displacement current opposes the applied e.m.f. and soon becomes equal to it so that the current falls to zero. When the electric "strain" of the dielectric is allowed to diminish, a current again exists momentarily in the opposite direction. Thus we see that a displacement current flows in the insulating material only when the applied e.m.f. is changing, but an alternating current gives rise to a changing e.m.f.; hence an alternating current can flow through a dielectric, the apparent resistance or **reactance** of the capacitance being zero when the frequency of the alternating current is infinite.

In making conductance measurements it is essential to use "pure sine wave" alternating current in order that no overtones will be present in the telephone (see page 54) when the fundamental note has been balanced out. Since the theory of alternating current, which is given in this chapter, assumes that the

current is sinusoidal, it is perhaps best to discuss at this point what is meant by current of sine wave form. If we plot the p.d. developed by an alternating-current generator as a function of time (Fig. 2), we find that the curve has the mathematical form of a sine wave providing that there are no overtones or harmonics other than the fundamental note. In Fig. 2 the values of the p.d. have been projected onto a circle whose revolving radius *OP* may be considered as representing the

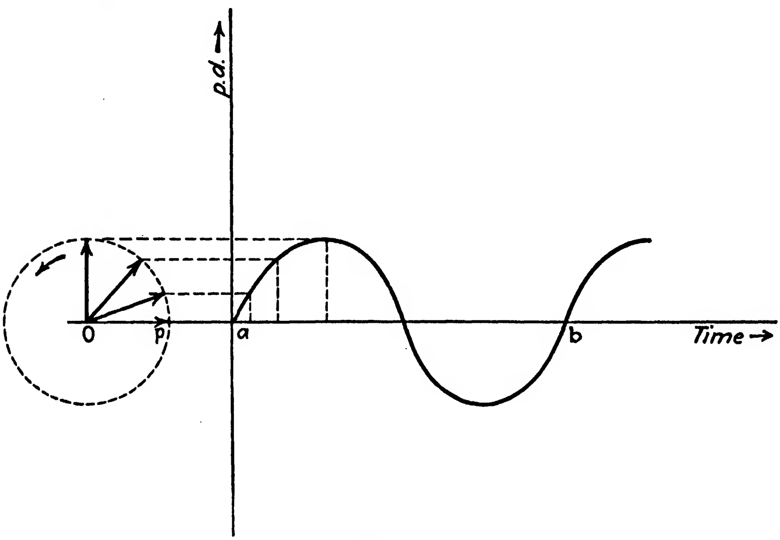

Fig. 2.

revolving conductor which cuts the magnetic lines of force of a dynamo. In the time of one complete cycle, represented by the distance *ab* and by the symbol τ, the radius *OP* completes a whole revolution, passing through the angle 2π radians. The angular velocity of *OP*, ω, is given by the equation

$$\omega = \frac{2\pi}{\tau}, \tag{9}$$

or by

$$\omega = 2\pi f \tag{10}$$

where f is the frequency of the alternating current.

In modifying Ohm's law to make it more applicable to alternating currents, we replace the resistance by a new quantity

called the **impedance.** Denoting the impedance by Z, Ohm's law becomes

$$I = \frac{E}{Z}. \tag{11}$$

The impedance is a function which includes both the direct-current resistance, the inductance, and the capacitance, the formal relationship being

$$Z = \sqrt{R^2 + X^2}, \tag{12}$$

where X is the reactance. The reactance is defined by the expression

$$X^2 = \left(\omega L - \frac{1}{\omega C}\right)^2 \tag{13}$$

for a circuit containing resistance, inductance, and capacitance in series as in Fig. 3. S is the source of e.m.f. in Fig. 3. In Eq. (13) L is the inductance and C is the capacitance (see Chap. VI for units and methods of measuring capacitance).

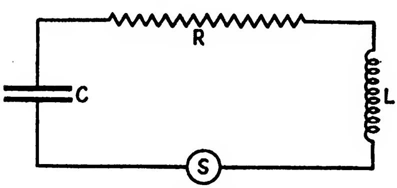

FIG. 3.—A circuit with inductance, resistance, and capacitance connected in series.

Although it would be out of place in this book to derive Eq. (11) on the basis of alternating-current theory, it will be possible to give some idea of the physical significance of the quantities, impedance, and reactance. Consider the circuit of Fig. 3. As the current flows across the resistance R there is a potential drop equal to IR and across the inductance and capacitance there is a potential drop equal to IX. One would expect that the total potential drop (p.d.) of the circuit would be equal to the sum of the p.ds. IR and IX, but this is not true, due to the fact that the two p.ds. are not in phase. To be in phase means that the maximum of the current and the maximum of the p.d. in a conductor occur at the same moment, and so on throughout the cycle. Actually the p.d. IX is passing through its maximum value when the current or p.d. IR is zero. If the voltage drop were measured across R and then across L and the two p.ds. added together, the sum would not be equal to the measured p.d. if the voltmeter were connected directly across the resistance

and inductance, *i.e.*, so as to include both R and L in its measurement. Actually it is found that the square of the total measured p.d. is equal to the sum of the squares of the two p.ds. measured separately, or

$$E^2 = (IR)^2 + (IX)^2 \tag{14}$$

or

$$I = \frac{E}{\sqrt{R^2 + X^2}} = \frac{E}{Z} \tag{15}$$

in agreement with Eqs. (11) and (12). (The capacitance C might equally well have been included in the p.d. measurements.)

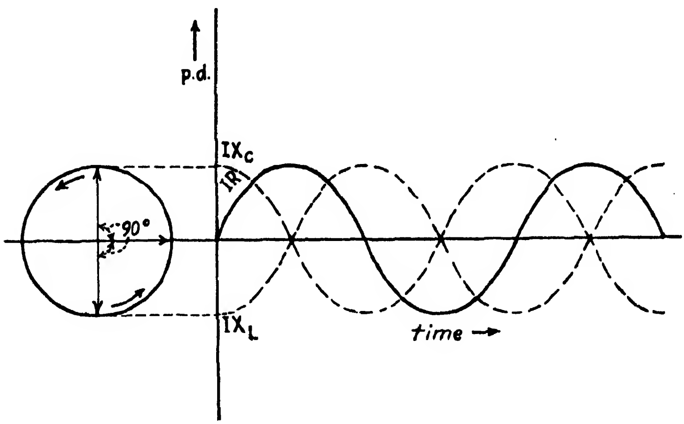

FIG. 4.

We now have to explain why the reactance due to capacitance $1/\omega C$ is subtracted from the inductive reactance ωL. The voltage on the condenser continually opposes the voltage on the inductance. We can say that in the case of the inductance the IX_L curve lies 90° "behind" the IR curve if the alternating values of IX_L and IR are plotted against time, while the IX_C curve for the condenser lies 90° "ahead" of the IR curve. The current-reactance curves* for the condenser and inductance are 180°

* Resistance, reactance, and impedance are frequently expressed in vector notation; thus

$$Z = R + jX,$$

where j is an operator and signifies that the angle between the scalars R and X is a right angle. If R is plotted horizontally and X vertically, we may call R the horizontal component of the impedance and X the vertical

apart, and the reactance of the first must be subtracted from the second, or

$$X_L - X_C = X. \tag{16}$$

The relationships between these various curves may be understood by reference to Fig. 4. Increase of frequency increases X_L, but decreases X_C. This is due to the fact that in the case of the inductance the back e.m.f. increases with increase of frequency. In the case of the condenser the current flows more easily through a condenser when the frequency is high; increase of frequency therefore reduces X_C.

The Alternating-current Wheatstone Bridge.—The most recent and most highly perfected resistance measuring apparatus is that of Jones and Josephs.* Their bridge is illustrated schematically in Fig. 6. It can be seen that the alternating-current bridge is fundamentally similar to the direct-current Wheatstone bridge, but a study of the conditions existing at bridge balance indicates in what respect the alternating-current bridge must differ from the direct-current bridge.

The bridge is assumed to be in balance when no current flows through the telephone, T, which serves to detect the passage of

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component. The inductive and capacitative reactances are plotted in opposite direction to each other; Fig. 5 illustrates these relationships for a series

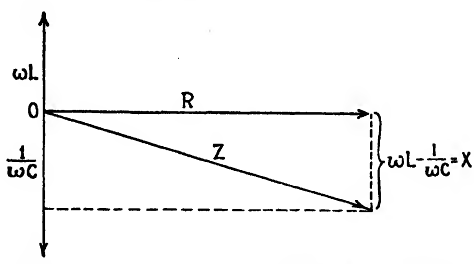

FIG. 5.—Vector diagram for inductance, capacitance, and resistance connected in series.

circuit in which the reactance due to capacitance is greater than that due to inductance.

* GRINNELL JONES and R. C. JOSEPHS, *J. Am. Chem. Soc.*, **50**, 1049 (1928). See also Jones and Bollinger, *ibid.*, **51**, 2407 (1929); **53**, 411, 1207 (1931); Jones and Bradshaw, *ibid.*, **55**, 1780 (1933); Jones and Christian, *ibid.*, **57**, 272 (1935); Jones and Mrs. Bollinger, *ibid.*, **57**, 280 (1935).

alternating current of audible frequency. If B and B' are at the same potential and if the potentials are in phase (that is, the potentials must be equal at every moment), $E_1 = E_3$ and $E_2 = E_4$; therefore

$$\frac{I_1Z_1}{I_2Z_2} = \frac{I_3Z_3}{I_4Z_4}. \tag{17}$$

If there is no leakage of current from any of the branches to ground or to other branches, I_1 will be equal to I_2 and I_3 will equal I_4 with the result that

$$\frac{Z_1}{Z_2} = \frac{Z_3}{Z_4}. \tag{18}$$

However, in the last section it was pointed out that an alternating current could flow through the best insulators; hence in the

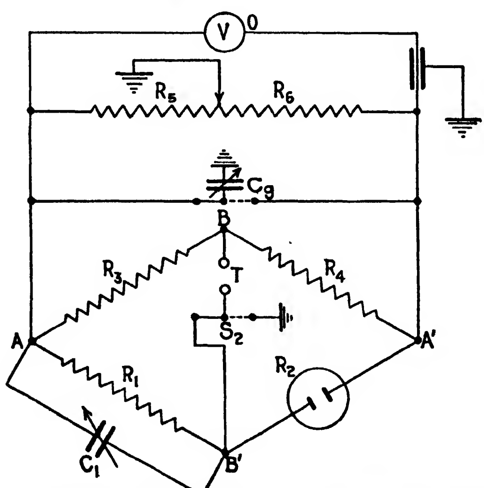

FIG. 6.—Schematic wiring diagram of the Jones and Josephs bridge.

alternating-current bridge there is very great danger that Eq. (18) will not be fulfilled at bridge balance. There are two general methods to overcome this danger; the method advocated by Jones and Josephs is to prevent current losses by moving objects away from the bridge. Since the capacity of a condenser is inversely proportional to the distance between the plates or approximately inversely proportional to the square of the dis-

tance between wires, it is evident that increasing the distance between the bridge arms and conducting objects will decrease the danger of escape of current from the bridge through capacitance to ground. Shedlovsky's* method is to screen his bridge arms carefully and symmetrically so that the current losses from the arms are symmetrical. His method has an additional advantage of screening the bridge from outside disturbances; for it is possible for the bridge to pick up currents due to induction from stray magnetic fields if it is not protected by screens. Magnetic fields are much more difficult to screen than are electrostatic fields. It is difficult to decide whether it is best to screen or not to screen a bridge; the answer probably lies in the experimental conditions existing in the particular laboratory where the bridge is set up. Among other precautions that should be observed in the design of the bridge is the necessity of the telephone being at ground potential. The method of achieving this in the proper manner will be described in a later paragraph.

If all the errors are eliminated or made negligible, we can say that†

$$I_1 = I_2 \qquad \text{and} \qquad I_3 = I_4 \tag{19}$$

and

$$\frac{Z_1}{Z_2} = \frac{Z_3}{Z_4}, \tag{18}$$

but

$$Z = \sqrt{R^2 + X^2},$$

hence

$$\frac{\sqrt{R_1^2 + X_1^2}}{\sqrt{R_2^2 + X_2^2}} = \frac{\sqrt{R_3^2 + X_3^2}}{\sqrt{R_4^2 + X_4^2}} \tag{20}$$

The relationship desired is

$$\frac{R_1}{R_2} = \frac{R_3}{R_4}, \tag{21}$$

and this is true only if

$$\frac{X_1}{R_1} = \frac{X_2}{R_2}$$

* T. Shedlovsky, *J. Am. Chem. Soc.*, **52**, 1793 (1930).

† See Jones and Josephs, *J. Am. Chem. Soc.*, **50**, 1068 (1928), for a more complete mathematical analysis of Eq. (20).

and

$$\frac{X_3}{R_3} = \frac{X_4}{R_4}. \tag{22}$$

A possible method of circumventing the difficulty inherent in Eq. (22) is to design the bridge and conductance cell in such a way that there are no reactances present, but this is impossible, particularly as regards the cell; hence there must be a variable condenser, C_1, inserted into the bridge to balance any capacity effects in the conductance cell R_2 and to restore the validity of Eq. (22).

The Vacuum-tube Oscillator.—In addition to the introduction of a variable condenser into the bridge, it is also necessary to provide a source of alternating current, a system for detecting the current, and a device for grounding the bridge. The very best source of sinusoidal alternating current is the vacuum-tube oscillator. The operation of this device depends upon the presence of a circuit containing inductance, capacity, and resistance in series (see Fig. 3). From Eq. (16) it is evident that when $\omega L = 1/\omega C$, the impedance Z is at a minimum and the current I is at a maximum. This condition for maximum current is called **resonance.** It is easy to calculate the frequency of the alternations of the current at resonance, for $\omega = 2\pi f$; hence

$$2\pi fL = \frac{1}{2\pi fC} \tag{23}$$

or

$$f = \frac{1}{2\pi\sqrt{LC}}. \tag{24}$$

Equation (24) shows the dependence of the frequency on the inductance and capacitance of the system in resonance and suggests how the frequency may be altered in any desired way by varying the inductance and the capacitance. The current at resonance is equal simply to E/R inasmuch as the reactance is balanced out.

It is possible to obtain a physical picture of resonance by comparing the electrical circuit with a mechanical system which can also exhibit the phenomenon of resonance. In Fig. 7, the spring represents the condenser and the mass the inductance; with the system originally at rest, a force is applied to the mass in

the horizontal direction. This force is opposed by the inertia of the mass, by the tension of the spring, and by the sliding friction, but the mass will move until the applied force is equal to the retarding tension of the spring. This point corresponds to the condenser being at its maximum charge. If the applied force is now removed, the spring will push the mass backward until the original position of the spring is attained. This is analogous to the potential on the condenser discharging until it becomes zero. But the mass has acquired a certain momentum and will continue to move to the left until the spring has been stretched in the opposite direction. The condenser in the electrical system would

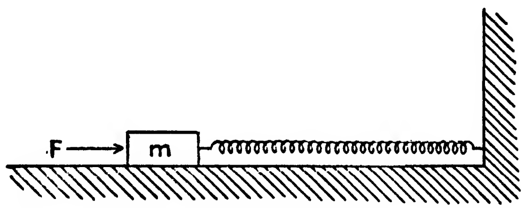

FIG. 7.—The mass and the spring can exhibit the phenomenon of resonance.

now be charged at a maximum value in the opposite direction due to the induced e.m.f. in the inductance. The tension on the spring next pulls the mass again to the right, and the whole process is once more repeated, without, however, the necessity for an external force to be applied again. At least no force would need to be applied further if the mass could slide back and forth without any mechanical friction. Similarly an electrical system oscillating in resonance would oscillate indefinitely provided there were no energy losses in either the inductance or the capacity. But it is impossible to construct such a perfect system; hence it is necessary to give the oscillating system a little "push" on every cycle to keep the oscillations going. This is the purpose of the vacuum tube in the vacuum-tube oscillator.

In Fig. 8 is illustrated a simple type of oscillator. F is the filament heated to a high temperature by the current from the A battery; the high temperature causes electrons to be ejected or to "evaporate" from the filament so that they stream in the direction of the positive plate, P, through the open meshwork grid, G. The plate is kept at a positive potential of 90 v. or so by

means of the battery B. The current from filament to plate can only go in one direction (the vacuum tube is a rectifier) and the magnitude of the current is largely dependent upon the potential of the grid *G*. The great control that the grid potential has upon the filament-plate current is due to the control the grid has upon the space charge that is built up by the electrons streaming between the filament and the plate. If the grid were not there, the magnitude of the current, at constant plate potential, would be limited by the space charge in the tube. Making the grid positive neutralizes the space charge and allows more electrons to stream to the plate. If the grid potential becomes negative in respect to the filament, the electrons are repelled from the grid in the direction of the filament, thereby building up the space charge and reducing the filament-plate current.

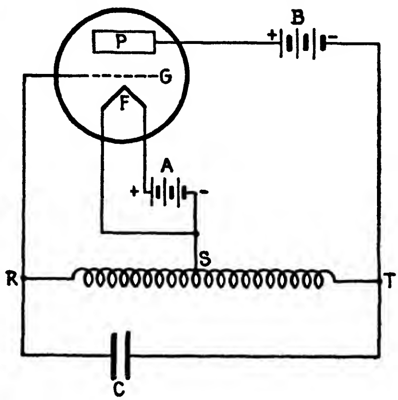

FIG. 8.—The vacuum tube as an oscillator.

When the connection to the filament from the A battery is made, electrons will stream to the plate and through the B battery around to the condenser *C* and also through the inductance from *T* to *S* and then back to the A battery again. While the condenser *C* is being charged, right-hand plate being negative, a current is induced in the inductance *RS* and will flow through *RS* to the A battery. This will cause the left plate of *C* and the grid to become positive which will then cause an even greater current to flow from filament to plate and to the condenser and through the inductance *ST*. This increase of current, however, will not go on indefinitely; and as soon as the rate of increase of current in *ST* begins to decline, the induced current in *RS* begins to decline also so that when the current is a maximum in *ST*, the induced current is zero in *RS*, and at the moment that the current begins to fall off in *ST*, the current in *RS* is in the opposite direction to its original motion. This means that the grid *G* is now becoming more negative, and also the condenser *C* will begin

to discharge; hence the current from the filament to plate will be considerably reduced and all the time that the left-hand plate of the condenser is negative, the filament to plate current will be very small. However, on the reverse of the current in the oscillating circuit, no current can flow back through the B battery to the plate since the vacuum tube only allows the current to flow from the plate through the B battery to T. Thus it is obvious that the energy given to the oscillating circuit on one half of the cycle cannot be taken back on the other half; hence the oscillating circuit receives intermittent electrical "pushes" which keep the current in oscillation. In the above discussion current flow is assumed to be electron flow. The vacuum tube illustrated in Fig. 8 is not quite so well adapted to audible frequencies (from 1,000 to 2,500 cycles per second are the customary frequencies) as is the oscillator used by Jones and Josephs, but it is somewhat simpler to understand. The current from this system can be picked up by a near-by or adjacent coil and delivered to the Wheatstone bridge. In Fig. 6 the source of the alternating current is designated by O. The oscillator is generally shielded from the bridge as are the leads from the oscillator to the bridge.

The Telephone.—The experimental technique in balancing the bridge consists in adjusting R_1 (Fig. 6) and C_1 until no current flows between the terminals B and B'. This minimum of current between B and B' is detected by listening for the minimum of noise in the telephone T. In the early days of conductance measurements (before 1919) the accuracy of the method depended to a considerable extent upon what the observer could hear in the telephone. Now, however, thanks to modern radio technique it is possible to amplify the current between B and B' so that the minimum can be detected very easily and with great sharpness. The first use of vacuum-tube amplifiers and the first use of the vacuum tube as an oscillator in conductance measurements we owe to Hall and Adams.*

Jones and Bollinger have recently discussed the principles of design of the amplifier and have suggested methods of increasing its sensitiveness. Let us consider, briefly, the fundamental principles involved in vacuum-tube amplification. The stream of electrons which flows between the filament and the plate in a

* Hall and Adams, *J. Am. Chem. Soc.*, **41**, 1515 (1919).

vacuum tube is very sensitive to the potential of the grid; any fluctuations in the grid potential cause corresponding fluctuations in the filament to plate current. From Fig. 9 it is evident that the current which flows from the grid to plate must be very small (the grid is cold and does not emit any thermionic electrons); hence a very small current is all that is required to change the grid potential appreciably. But a comparatively large current flows from the filament to plate through B, R, and back to the filament; therefore the current entering the tube from the bridge has been considerably amplified. The amplified current may be still further amplified by impressing the current picked up in S upon the grid of a second vacuum tube. This amplification cannot be carried on indefinitely, however, owing to the fact that any extraneous currents are amplified as well as the true bridge current.

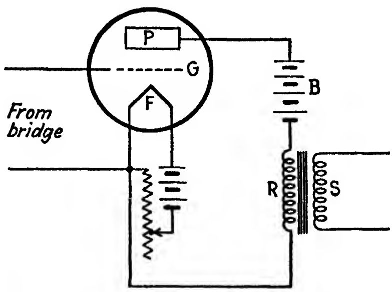

FIG. 9.—The vacuum-tube amplifier.

The Method of Grounding the Telephone.—In using the telephone there is the danger that a capacitance may be introduced between the telephone coils and observer, who is at ground potential. This would cause a loss of current from the bridge and would also prevent a sharp minimum; hence it is advisable to maintain the telephone circuit at earth potential, but not directly connected to earth. This is accomplished in the Jones and Josephs bridge by means of an adaptation of the Wagner ground.*

The telephone is connected temporarily to ground at S_2 (Fig. 6). R_5 and R_6 and C_g are varied until a minimum is obtained in the telephone; the telephone is then disconnected from the earth, but it remains at the earth potential. This adjustment is made after R_1 and C_1 have been adjusted as closely as possible to their proper settings. After the telephone has been adjusted to the earth's potential, it is connected to the bridge proper again, and R_1 and C_1 adjusted to their final values. In this way it is possible to bring the bridge to balance with the

* WAGNER, *Elektrotechnische Z.*, **32**, 1001 (1911).

telephone at the earth's potential without any danger of loss of current from the bridge by connecting the telephone directly to ground.

Resistance Boxes and Conductance Cells.—In order to measure the resistance of the unknown cell R_2 (Fig. 6), it is, of course, necessary to have a standard variable resistance at R_1. Furthermore, R_3 and R_4 must be equal, and all the resistances, R_1, R_3, and R_4 should give the same values with direct current as with alternating. Jones and Josephs give the specifications of an ideal resistance box and describe in detail how these requirements may be most nearly met. The electrochemist, however, rarely has the time to build or to have built special resistance boxes and generally buys whatever is available on the market. Good resistance boxes are becoming more and more available as methods for improving their performance are worked out.

A very important consideration in making conductance measurements is the proper design of cell. The total resistance of the cell should not be lower than 1,000 ohms on account of an effect at the electrodes called polarization (to be discussed in Chap. XXVIII) which introduces errors if the total resistance falls below 1,000 ohms. The maximum total resistance should not be greater than 50,000 ohms, because alternating-current errors increase as the square of the resistance being measured. For metallic conductors and also for electrolytic conductors, it will be remembered that

$$R = \frac{1}{\kappa}\frac{l}{A}, \tag{25}$$

where κ is the specific conductance, l the length of the conductor, and A the area of cross section. Electrolytes have very widely varying values of κ; hence, if R must always be greater than 1,000 and less than 50,000, it is evident that l/A must vary. In other words, one conductance cell is not suitable for all electrolytes; it is necessary to have a number of cells all with different cell constants, l/A, in order to be able to measure the conductance of electrolytes having widely different specific conductances. A usual type of conductance cell, known as the Washburn pipet type, is illustrated in Fig. 10. By making the cell longer or shorter, wider or narrower, the cell constant is varied at will.

Narrow cells are preferable to wide cells because they come more quickly to temperature equilibrium in the constant temperature bath. (It must be remembered that the resistance of a solution depends upon the temperature.) In Fig. 10, P and P' are two platinum electrodes which conduct the current into and out of the solution which is contained in the main body of the cell. Side arms H and H' are filled with mercury which makes contact with the platinum electrodes. The leads to the bridge dip into the mercury, thus making contact with the cell. The cell is filled by sucking or forcing the solution in at S'. A new cell is prepared for use by careful cleaning (after the metallic electrodes are covered with a surface of platinum black) and is then steamed out for a day or so and finally allowed to age for some time. Before use it is rinsed several times with the solution whose conductance is to be measured, and after one measurement has been taken, it is advisable to refill the cell with the same solution to see if the original reading can be duplicated. Cells used to measure the conductance of pure water generally have large bright platinum electrodes uncovered with platinum black. Conductance cells are preferably made of chemical resistant glass, and for the most refined measurements quartz cells have been used.

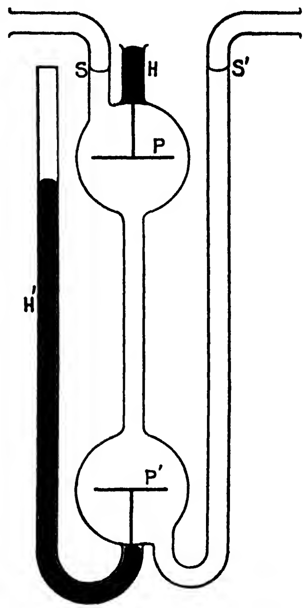

FIG. 10.—Washburn pipet conductance cell.

In order to calculate the specific conductance from Eq. (25) it is necessary to know the value of the cell constant l/A but this is quite impossible of determination by making actual measurements of the length and area of cross section of a cell like the one illustrated in Fig. 10. If the value of the specific conductance of a single solution is known, this solution can be inserted into the cell, and a single determination of R will allow l/A to be calculated. This is the usual practice, most conductance measurements being based on the absolute value of the specific

conductance of several potassium chloride solutions which were accurately determined many years ago by Kohlrausch. It is to be expected that modern developments in conductance technique such as the introduction of vacuum-tube amplifiers, oscillators, better resistance boxes, etc., would enable electrochemists to measure the absolute specific conductances with a higher degree of accuracy than Kohlrausch was able to. However, new absolute values obtained by Jones and Bradshaw* indicate that the Kohlrausch values are surprisingly accurate, more accurate than the Parker and Parker† absolute standards accepted by the "International Critical Tables." Jones and Bradshaw's data are given in Table I. The concentration is expressed in demal units; a one demal solution is defined as one gram molecule of salt dissolved in one cubic decimeter of solution at 0°C., or 76.6276 g. of potassium chloride dissolved in 1,000 g. of water both weighed in air. Tenth and hundredth demal solutions contain 7.47896 and 0.746253 g. of potassium chloride per 1,000 g. of water (all weighed in air), respectively.‡

TABLE I.—ABSOLUTE SPECIFIC CONDUCTANCE OF POTASSIUM CHLORIDE SOLUTIONS IN OHM^{-1} CM.$^{-1}$
(*Jones and Bradshaw*)

Demal concn.	0°	18°	25°
1.0	0.065176	0.097838	0.111342
0.1	0.0071379	0.0111667	0.0128560
0.01	0.00077364	0.00122052	0.00140877

The use of a single solution as an absolute standard depends upon the assumption that the value of the cell constant is independent of the solution which is being measured. As a matter of fact, Parker§ discovered in 1923 that this was not strictly true; the deviation from constancy amounting to as much as 0.33 per cent. Since Jones and Josephs found that they could balance their bridge with an error of only 0.001 per cent, the error

* GRINNELL JONES and B. C. BRADSHAW, *J. Am. Chem. Soc.*, **55**, 1780 (1933).

† H. C. PARKER and E. W. PARKER, *J. Am. Chem. Soc.*, **46**, 312 (1924).

‡ This is the only place in this textbook where the demal concentration unit is used.

§ H. C. PARKER, *J. Am. Chem. Soc.*, **45**, 1366, 2017 (1923).

found by Parker (called the Parker effect) is appreciable. Jones and Bollinger,* however, have recently discovered the cause of the Parker effect and give details for overcoming the difficulty. Referring to Fig. 10, it can be seen that there is a possible current bypass or short circuit between *H* and *S'*. Alternating current entering the cell at *H* can flow through the glass dielectric and through the bath liquid to *S'*, down *S'* and out through *H'* without passing between the electrodes *P* and *P'*. This is the cause of the Parker effect and is overcome very simply by designing the cell so that *H* and *S'* are far apart as in Fig. 11. Jones and

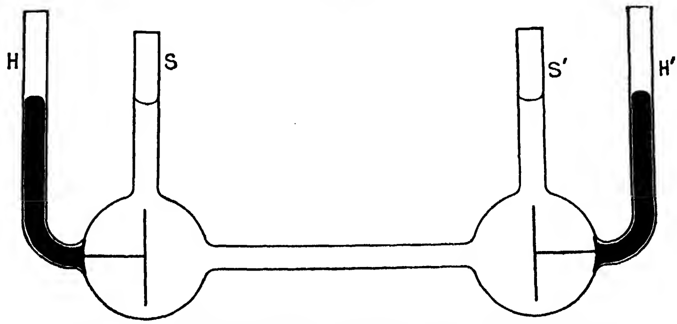

FIG. 11.—The Jones and Bollinger type conductance cell.

Bollinger point out that cells of the type recommended by them are reliable within 0.01 per cent and give resistances which are practically independent of the frequency of the alternating current.

Jones and Josephs also discovered that a nonconducting paraffin oil as the bath liquid gave much better results than water. Hence all conductance measurements should be made with the cell immersed in an oil constant-temperature bath. For the finest work the temperature should be controlled as well as possible, preferably to 0.001°C.

The Preparation of Solutions for Conductance Measurements.—The final accuracy of a conductance measurement often depends upon the care with which the salts and water are purified and the precision with which the solutions are made up inasmuch as the electrical technique has been developed to such a high state of perfection. Salts may be purified in a number of ways

* GRINNELL JONES and G. M. BOLLINGER, *J. Am. Chem. Soc.*, **53**, 411 (1931).

such as by synthesis from other pure compounds, precipitation or recrystallization from water or other solvents and by separation of the salts from the mother liquor in mechanical centrifuges. The most common impurity in the salt is water, but this may be eliminated by fusion of the solid, preferably in a "Richards bottling apparatus" if the salt decomposes or hydrolyzes when heated in air.* The Richards bottling apparatus, illustrated in Fig. 12, enables a salt such as a chloride to be heated or fused in any desired atmosphere such as dry hydrogen chloride. In this way, a salt can be dried without decomposition and weighed without exposure to air. The salt is placed in a platinum boat, heated, and after cooling it is pushed with a glass rod into the weighing bottle *W* at the left. The apparatus is tilted slightly

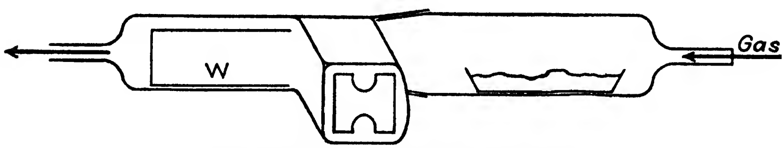

FIG. 12.—Richards bottling apparatus.

so that the weighing bottle stopper can run down into the tube. The stopper is then pushed into place, the apparatus taken apart, and the weighing bottle containing the salt in the boat finally weighed.

The purification, storage, and handling of the water present more serious difficulties. Ordinary distilled water is not suitable for conductance measurements because it contains dissolved gases such as carbon dioxide, ammonia, hydrogen chloride, etc., which give to it an appreciable conductance. It is necessary to reduce the conductance of water to as low a value as possible in order that the experimental measurement of the conductance may measure as far as possible the conductance due to the added salt and not that due to the water. The specific conductance of a $0.0001c$ potassium chloride solution is 12.9×10^{-6} ohm^{-1} cm.$^{-1}$ or mho while that of ordinary distilled water is around 2×10^{-6} mho; hence in this case the conductance due to the water would be about 15 per cent of the total which is far too

* T. W. RICHARDS and H. G. PARKER, *Proc. Am. Acad. Arts Sci.*, **32**, 59 (1896).

great. As the salt becomes more concentrated, the specific conductance due to the water becomes relatively smaller; so that at a concentration of 0.1*c* the conductance of the water may be neglected.

In the recent excellent work of Shedlovsky* on the conductance of various salts at concentrations as low as 0.00003*c*, the water was purified by the distillation of ordinary distilled water from an alkaline potassium permanganate solution in a specially designed still.† In this still the vapor passes through a settling chamber where traces of spray separate from the steam. The steam next goes to a condenser where it is only partially condensed; it is assumed that all dissolved gases are carried off in the uncondensed vapor. The specific conductance of this water was found to vary between 0.1×10^{-6} and 0.4×10^{-6} mho; these values represent the best results that can be obtained by a single redistillation. Kohlrausch and Heydweiller‡ obtained water with a conductance of 0.043×10^{-6} mho after forty-two distillations in vacuo at a low temperature.

After purification of the water Shedlovsky poured 950 cc. of the water into a specially designed cell, bubbled purified nitrogen through to remove any gases that might have dissolved in it, and measured the conductance of the water between the platinum electrodes that were contained in a side arm of the bottle. This figure gave the specific conductance due to the water. Without changing anything the stopper of the flask was removed, and a small amount of salt added to the water. After solution of the salt and mixing of the solution by bubbling nitrogen, the conductance of the solution was measured once again between the electrodes in the side arm. This gave the specific conductance of the solution which after subtraction of the specific conductance due to the water enabled the specific conductance due solely to the salt in the water to be calculated. In this way, the error due to the conductance of the pure water is largely eliminated.

For concentrations above 0.0005*c*, Shedlovsky measured the conductance of the water in a separate cell, made up his solution in a flask by weighing into the flask a definite weight of salt and

* T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1411 (1932).

† Kraus and Dexter, *J. Am. Chem. Soc.*, **44**, 2469 (1922).

‡ See Bencowitz and Hotchkiss, *J. Phys. Chem.*, **29**, 705 (1925).

water, and calculated the concentration to the volume molal basis by means of the known densities of the solutions. The salt solution was then transferred to a cell having a suitable cell constant and the conductance determined.

The Calculation of the Molal Conductance from the Resistance Measurement.—It is perhaps well to review the procedure necessary to calculate the molal conductance from the resistance measurement. Let us start with a new cell whose cell constant is unknown, place into this cell a 0.1 demal potassium chloride solution whose specific conductance is 0.0128560 mho (Table I) and then measure the resistance of the cell. Let us assume that the resistance is 3991.90 ohms. The specific conductance of the potassium chloride solution is 0.0128560 + 0.0000012 or 0.0128572. (The small correction is due to the conductance of the water.) Since

$$\frac{l}{A} = \kappa R,$$

the cell constant of the unknown cell is

$$\frac{l}{A} = (3{,}991.90)(0.0128572) = 51.2066.$$

Let us now place in the cell a 0.05*c* solution of some salt made up from water having a specific conductance of 2.2×10^{-6} mho. If the measured resistance (corrected for any resistance box error) of the cell filled with the new solution is 4,888.20, the specific conductance is given by the equation

$$\kappa = \frac{l/A}{R} = \frac{51.2066}{4{,}888.20} = 0.0104756.$$

From this value of the specific conductance of the solution the conductance due to the water must be subtracted, giving as the specific conductance due solely to the salt in the solution, 0.0104734 mho. The molal conductance is calculated by the equation

$$\bar{\Lambda} = \frac{1{,}000\kappa}{c} = \frac{(1{,}000)(0.0104734)}{0.05} = 209.47.$$

The equivalent conductance would be obtained by dividing $1{,}000\kappa$ by the normality. It should be pointed out that the

conductance calculations are simplified if a direct-reading resistance bridge is used. The conversion of measured ratios into resistances is laborious, particularly if a large number of measurements have to be so converted.

The Use of Conductance Measurements Other Than to Measure the Molal Conductance.—Conductance measurements are of primary importance in helping to determine the nature of solutions, but sometimes it is possible to use to advantage the resistance reading of the bridge directly without the necessity of calculating the molal conductance. In the titration of a strong

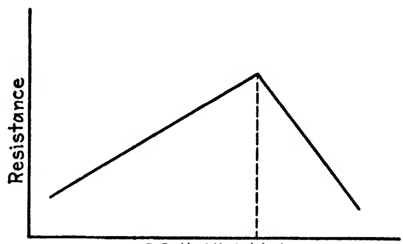

FIG. 13.

acid with a strong base, the resistance of the solution is a maximum at the end point. The hydrogen and hydroxyl ions have a greater conductance than any other ion, and when they are removed from the solution to form water, the resistance increases. After the end point has been reached and either alkali or acid is added in excess, the resistance diminishes. The course of the titration is illustrated in Fig. 13; the sharp maximum indicates the end point of the titration. For details concerning conductimetric titrations of weak acids with strong bases or *vice versa* the reader is referred to the monograph by Kolthoff.* Resistance measurements may also be applied to analyses in which precipitates are formed, provided the conductance due to the salt formed in the reaction is sufficiently different from that of the salt originally present in the solution.

If the molal conductance is known, the measurement of the specific conductance enables the concentration to be calculated.

* I. M. KOLTHOFF, "The Colorimetric and Potentiometric Determination of pH," 133*ff*., John Wiley & Sons, Inc., New York, 1931. See also H. T. S. BRITTON, "Conductometric Analysis," Chapman and Hall, Ltd., London, 1934.

The solubility of sparingly soluble salts is determined in this way as is also the dissociation constant of water (see Chap. XXI). Conductance measurements have also been used to determine the concentration of many other types of solutions.

Exercises

1. Calculate the cell constants of the following cells: (*a*) length 6 cm., *A* 1 sq. cm.; (*b*) length 0.1 cm., *A* 2 sq. cm.; (*c*) length 25 cm., *A* 1.5 sq. cm.; (*d*) a cell in which one demal potassium chloride solution gives a resistance at 25° of 5.258 ohms; (*e*) a cell in which one-hundredth demal potassium chloride gives a resistance of 27, 682 ohms also at 25°.

2. Some water used in a conductance measurement had a specific conductance at 25° of 0.8×10^{-6} mho. What percentage of the specific conductance of the one and one-hundredth demal potassium chloride solutions is this water conductance?

3. What is the specific conductance of a solution that gives a resistance of 2,682 ohms in a cell with cell constant equal to five? If the solution was made up using water of specific conductance equal to 1.2×10^{-6} mho, what is the corrected specific conductance of the solution?

4. A 0.001 *c* barium chloride solution has a specific conductance of 2.6×10^{-4} mho. What is its molal conductance? What is its equivalent conductance?

5. Draw a diagram of the Jones and Josephs bridge. If the two standard ratio arms were not exactly equal, how could the resistance of an unknown cell be calculated? What is the advantage of a direct reading resistance bridge over the old type of bridge in which the bridge was balanced by changing the ratio between branches R_3 and R_4 in Fig. 6?

6. Calculate the frequency of the alternating current supplied by a circuit whose inductance is equal to 0.1 henry and whose capacitance is equal to 1×10^{-6} farad (the farad is the unit of capacitance) when the current in the circuit is at resonance.

7. What is the capacitance necessary to give a frequency of 1×10^6 if the inductance of the resonating circuit is equal to 1×10^{-3} henry?

8. Prove that

$$\frac{R_1}{R_2} = \frac{R_3}{R_4}$$

if

$$\frac{\sqrt{R_1^2 + X_1^2}}{\sqrt{R_2^2 + X_2^2}} = \frac{\sqrt{R_3^2 + X_3^2}}{\sqrt{R_4^2 + X_4^2}},$$

$$\frac{R_1}{X_1} = \frac{R_2}{X_2},$$

and

$$\frac{R_3}{X_3} = \frac{R_4}{X_4}.$$

CHAPTER V

THEORETICAL INTERPRETATION OF THE CONDUCTANCE OF ELECTROLYTES. I

Units, Definitions, and Equations of Motion of an Ion.—The conduction of electricity in a solution is due to the motion of charged bodies. Electrical conductors may be divided into two main classes, metallic conductors or *conductors of the first class* in which electrons only move, and electrolytic conductors or *conductors of the second class* in which positive or negative ions or both of them move. In second-class conductors the passage of electricity is always accompanied by the transport of matter in contrast to first-class conductors in which no matter migrates. (A possible exception to this is the migration of the proton in platinum as mentioned in Chap. III.) Metallic conductors have a far greater conducting power than do electrolytic conductors; the specific conductance of silver is 6×10^5 ohms^{-1} cm.$^{-1}$, which is over a million times greater than the specific conductance of most solutions. The conducting power of metals decreases with rise of temperature while exactly the opposite effect is observed in the case of electrolytes. Metallic conductors are opaque while electrolytic conductors are usually transparent. Metallic conductors can be distinguished from electrolytic conductors by these properties, although there have been discovered transition conductors, such as sodium in liquid ammonia (Franklin, Kraus, Cady), which have properties halfway between the two types.

Electrolytic conductors may be liquid or solid; we shall be chiefly concerned with the electrical conductance of liquid solutions, particularly of aqueous solutions. Electrolytes are called either *strong* or *weak electrolytes* depending upon their ability to conduct the current well or comparatively poorly. This classification is not very satisfactory, however, as there are numerous electrolytes that are neither strong nor weak but are transition electrolytes. We shall limit weak electrolytes usually to those for which a dissociation constant can be calculated.

The motion of ions in solution is retarded by the viscosity of the medium and by opposing eecltrical forces. If it is recalled how slowly a colloidal precipitate sinks, it will be realized that such extraordinarily fine particles as the ions require an enormous force to move them through the solution with any appreciable velocity. Let us consider an ion in a solution that is so dilute that other ions have no effect upon the motion of the ion in question. If a potential difference is applied to two electrodes which are immersed in the solution, the ion which we are considering will begin to move and will accelerate until the applied external force, Xq_i, is equal to the retarding force. X is given by the equation (ψ is electric potential)

$$X = -\frac{\partial \psi}{\partial x} \tag{1}$$

and q_i is the charge on the ion (the subscript i refers to the ith ion, any ion that may be chosen). If m_i is the mass of the ion and a its acceleration,

$$m_i a = Xq_i = m_i \frac{d^2x}{d\tau^2}, \tag{2}$$

Multiplying by dx, we obtain

$$Xq_i dx = m_i dx \frac{d^2x}{d\tau^2} = d\left[\frac{m_i}{2}\left(\frac{dx}{d\tau}\right)^2\right]$$

but

$$\frac{dx}{d\tau} = \bar{v}_i, \tag{3}$$

where $\bar{v}_i$ is the velocity of the ith ion; hence

$$Xq_i dx = d(\tfrac{1}{2}m_i\bar{v}_i^2). \tag{4}$$

If $k\bar{v}_i$ is the retarding force of friction, the acceleration of the ion is given by the equation,

$$m_i \frac{d^2x}{d\tau^2} = Xq_i - k\bar{v}_i; \tag{5}$$

also

$$d\left(\frac{m_i}{2}\bar{v}_i^2\right) = (Xq_i - k\bar{v}_i)dx. \tag{6}$$

When X is constant, $\bar{v}_i$ will increase until the accelerating force Xq_i equals the retarding force, $k\bar{v}_i$; then

$$\bar{v}_i^0 = \frac{Xq_i}{k}. \tag{7}$$

Stokes has calculated mathematically that the velocity, $\bar{v}_i^0$, of a sphere of radius, r_i, in a stationary medium of viscosity η is given by the expression

$$\bar{v}_i^0 = \frac{f}{6\pi\eta r_i}, \tag{8}$$

where f is the accelerating force on the particle. We do not know to what extent Eq. (8) is applicable to ions. Rearranging Eq. (6), we get the equation

$$Xq_i dx = \text{work done} = d\left(\frac{m_i}{2}\bar{v}_i^2\right) + k\bar{v}_i dx, \tag{9}$$

which shows that the work done by the external force Xq_i goes partly to produce kinetic energy and partly to do work against friction. The heat developed by the constantly moving ion against the force of friction may easily be calculated by integrating the following integral from 0 to x and from 0 to τ,

$$\int_0^x k\bar{v}_i^0 dx = \int_0^\tau k\bar{v}_i^{0\,2} d\tau = \int_0^x Xq_i dx.$$

The result is

$$\bar{v}_i^{0\,2} k\tau = \text{heat developed}, \tag{10}$$

which is analogous to the equation

$$I^2 R\tau = \text{joules}.$$

Equation (7) is also analogous to the equation $I = E/R$. The time necessary for the ion to reach its steady velocity, $\bar{v}_i^0$, may readily be calculated. Rewriting Eq. (6) as

$$\frac{d\bar{v}_i}{Xq_i - k\bar{v}_i} = \frac{d\tau}{m_i}$$

and integrating between $\tau = \tau$ and $\tau = 0$, we have

$$\bar{v}_i = \frac{Xq_i}{k}\left(1 - e^{-\frac{k\tau}{m_i}}\right). \tag{11}$$

Equation (11) shows that the ion reaches its steady velocity $\bar{v}_i^0 = Xq_i/k$ very quickly inasmuch as in the case of ions k is large and m_i is small.

The **mobility** of an ion is numerically equal to its velocity when X is equal to unity. The mobility of a positive ion in centimeters per second is commonly designated by u and that of a negative ion by v when the potential gradient is expressed in volts per centimeter.

The specific conductance of a solution is equal to the sum of the conductances due to the separate ions since, as was first pointed out by Kohlrausch,* the conductances may be assumed to be additive. The specific conductance due to the positive ions of a binary salt is equal to the product of the mobility of the ion, the charge on the ion (expressed in coulombs) and the number of ions per cubic centimeter, or

$$\kappa_+ = n_+ q_+ u; \tag{12a}$$

similarly

$$\kappa_- = n_- q_- v. \tag{12b}$$

The number of ions of any one kind per cubic centimeter in terms of the stoichiometrical concentration c (moles per liter of solution) is

$$n_i = \frac{c}{1{,}000}\alpha \mathbf{N} \nu_i, \tag{13}$$

where α is the degree of dissociation [Chap. II, Eq. (1)]. $\mathbf{N}$ is Avogadro's number and ν_i is the number of ions of the ith kind that one molecule of the salt dissociates into. The charge on the ith ion in terms of its valence and the faraday is

$$q_i = \frac{z_i F}{\mathbf{N}} \tag{14}$$

(the valence of a negative ion is to be taken numerically as positive unless otherwise stated). Substituting Eqs. (13) and (14) into (12a) and (12b), we obtain

$$\kappa_+ = \frac{c}{1{,}000}\, \alpha \nu_+ z_+ F u, \tag{15a}$$

$$\kappa_- = \frac{c}{1{,}000}\, \alpha \nu_- z_- F v. \tag{15b}$$

The molal conductance is given by the equation

$$\bar{\Lambda} = \frac{1{,}000\kappa}{c}, \tag{IV-4}$$

* KOHLRAUSCH, *Wied. Ann.*, **6**, 1 (1879); **26**, 161 (1885).

or since

$$\kappa = \kappa_+ + \kappa_- = \frac{c}{1{,}000} \alpha \nu z F(u + v), \tag{16*}$$

$$\bar{\Lambda} = \alpha \nu z F(u + v). \tag{17}$$

For the equivalent conductance we have

$$\Lambda = \alpha F(u + v), \tag{18}$$

since

$$\frac{\bar{\Lambda}}{\nu z} = \Lambda.$$

Equations (17) and (18) are important equations.

The ionic equivalent conductances follow immediately from Eq. (18)

$$\Lambda_+ = \alpha F u \tag{19a}$$

and

$$\Lambda_- = \alpha F v. \tag{19b}$$

The ionic molal conductances are defined by the equations,

$$\bar{\Lambda}_+ = \alpha z_+ F u \tag{20a}$$

and

$$\bar{\Lambda}_- = \alpha z_- F v. \tag{20b}$$

Experimental Results of Conductance Measurements.—Before considering the theories which have been developed to explain the results of the conductance measurements, it is well to examine the experimental data in order to see how the conductances of different electrolytes vary with the concentration, dielectric constant, viscosity, temperature, and pressure. The change of conductance with change of concentration has been most extensively studied since the conductance is chiefly a function of the concentration. It is customary to express the data in terms of the equivalent conductance, *i.e.*, the conductance of a solution containing one equivalent of solute when the solution is placed between electrodes 1 cm. apart. Table I contains data for the equivalent conductance of two typical strong electrolytes, hydrochloric acid and potassium chloride, and of one weak electrolyte, acetic acid. The important facts to notice from

* Equation (16) follows from (15*a*) and (15*b*) because $\nu_+ z_+$ is always equal to $\nu_- z_-$ due to the fact that solutions are electrically neutral.

TABLE I.—EQUIVALENT CONDUCTANCES OF AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE, HYDROCHLORIC ACID, AND ACETIC ACID AT 25°C.

c	Λ_{KCl}	Λ_{HCl}	c	Λ_{HOAc}
0.001	147.4	421.38	0.000111	127.7
0.002	146.3	419.17	0.00103	48.133
0.005	143.8	415.11	0.002414	32.208
0.01	141.18	411.08	0.005911	20.956
0.02	138.04	406.07	0.01283	14.371
0.05	133.1	397.8	0.02	11.563
0.1	128.6	389.8	0.05	7.356
0.2	123.9	379.6	0.1	5.20
0.5	117.2	359.2	0.2	3.650
1.0	111.86	332.8		

Table I are that all the equivalent conductances decline with rising concentration and that the equivalent conductances of the two strong electrolytes do not change nearly so much with change of concentration as do the equivalent conductances of the weak electrolyte, acetic acid. The sharp decline of the equivalent conductance in dilute solutions is characteristic of weak electrolytes. One finds by indirect methods that at zero concentration acetic acid has a much greater conductance than potassium chloride, the values being 390.59 and 149.82, respectively. Electrolytes which contain either the hydrogen ion or hydroxyl ion are relatively good conductors unless the electrolyte is a weak electrolyte.

Not only can we classify electrolytes as strong or weak electrolytes or as neutral electrolytes or electrolytes containing the hydrogen and hydroxyl ions, but we can also classify strong electrolytes according to the valence of the ions present. The equivalent conductances of two chlorides having a monovalent cation, a divalent cation and a trivalent cation, are given in Table II, and it can easily be seen that the conductances of the electrolytes containing the ions of high valence decline more rapidly with increase of concentration than do the conductances for the two monovalent salts. There is evidently a valence effect which must be considered in any theory of conductance measurements.*

*Data of Tables I and II from the "International Critical Tables."

TABLE II.—EQUIVALENT CONDUCTANCES OF SOME STRONG ELECTROLYTES AT 25°C.

c	Λ_{NaCl}	Λ_{KCl}	Λ_{SrCl_2}	Λ_{BaCl_2}	Λ_{AlCl_3}	Λ_{LaCl_3}
0.001	124.1	147.4	132	134	144	132
0.002	123.0	146.3	129	132	136	128
0.005	120.8	143.8	124	128	125	121.6
0.01	118.6	141.18	119	123.7	118	115.9
0.02	115.8	138.04	115	119.2	110	109.7
0.05	111.0	133.1	108	111.7	100	101.3
0.1	106.6	128.62	103	105.3	92	94.6

The equivalent conductances of weak electrolytes vary widely from solute to solute, but they all have the common property of being quite large at zero concentration and falling more or less rapidly as the concentration increases. Table III includes the equivalent conductances of three weak electrolytes, acetic acid, formic acid, and cyanoacetic acid.

TABLE III.—EQUIVALENT CONDUCTANCES OF ACETIC, FORMIC, AND CYANOACETIC ACIDS[a]

Acetic acid, 25°C.		Formic acid, 18°C.		Cyanoacetic acid, 25°C.	
c	Λ	c	Λ	c	Λ
0	387.9	0	364.5	0	386.1
0.0002879	86.71	0.001052	124.9	0.0002322	364.8
0.0005757	63.60	0.001923	97.92	0.0003757	353.2
0.001151	46.13	0.003855	72.51	0.0004644	347.1
0.002303	33.22	0.004161	70.21	0.0007515	329.2
0.004606	23.81	0.008809	50.07	0.0009287	320.0
0.009208	16.98	0.01595	37.93	0.001503	294.9
0.01842	12.091	0.03208	27.36	0.001858	282.6
0.03685	8.591	....	......	0.003005	252.4
0.07369	6.086	....	......	0.003716	238.7

[a] Data taken from Davies, "The Conductivity of Solutions," pp. 11 and 91, Chapman and Hall, London, 1930.

It is characteristic of aqueous solutions that the equivalent conductance continually declines as the concentration increases, but if we examine nonaqueous solutions, particularly solutions formed of solvents having very low dielectric constants, we find

that the equivalent conductance-concentration curve may exhibit both minima and maxima. The equivalent conductance of potassium iodide in liquid sulfur dioxide* at 0°C. has a minimum value at 0.1 N and a maximum value at 1.0 N (the equivalent conductance is also a maximum at zero concentration).

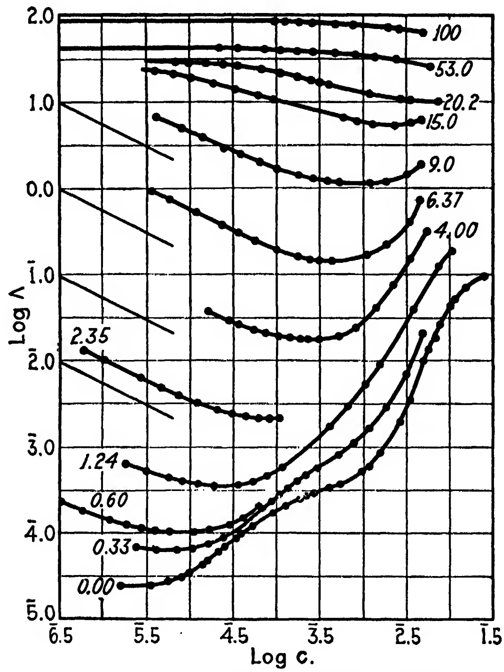

FIG. 1.—Tetraisoamylammonium nitrate in dioxane-water mixtures. (Weight per cent of water given opposite corresponding curve.)

The effect on the equivalent conductance of lowering the dielectric constant of the medium is beautifully illustrated by the recently published data of Kraus and Fuoss.†

Figure 1 illustrates the equivalent conductance of tetraisoamylammonium nitrate in dioxane-water mixtures as a function

* FRANKLIN, *J. Phys. Chem.*, **15**, 683 (1911).

† C. A. KRAUS and R. M. FUOSS, *J. Am. Chem. Soc.*, **55**, 21 (1933). Other papers of this series entitled, "Properties of Electrolytic Solutions" are: FUOSS and KRAUS, *J. Am. Chem. Soc.*, **55**, 476, 1019, 2387, 3614 (1933); KRAUS and HAWES, *ibid.*, **55**, 2776, (1933); KRAUS and KAHLER, *ibid.*, **55**, 3537 (1933); KRAUS and JOHNSON, *ibid.*, **55**, 3542 (1933).

of the salt concentration. The separate curves represent the conductances in different solvents, the solvents varying between 100 per cent water and 100 per cent dioxane. The dielectric constant of pure water is 78.6 and that of dioxane is 2.2. The top curve is typical of the equivalent conductance of a strong electrolyte in water, the equivalent conductance decreases comparatively slowly as the concentration increases. Since logarithms are plotted, any small change does not show up on the graph. As the dielectric constant of the medium is decreased by decreasing the water content, not only is the absolute magnitude of the equivalent conductance materially reduced, but the equivalent conductance becomes much more dependent upon the concentration and more like the conductance of a weak electrolyte. When the percentage of water in the solvent has fallen to 15 (dielectric constant equal to 9), a minimum in the equivalent conductance appears, and as the percentage of water falls still lower, the minimum in the curve shifts to lower concentrations. Finally, at zero per cent water, the equivalent conductance minimum occurs at such a low concentration that Kraus and Fuoss could not observe it. It can also be noticed that as the water content decreases, the eccentricities of the conductance curves become more pronounced.

The equivalent conductances of metals and salts dissolved in liquid ammonia are particularly interesting and will be discussed in a later chapter.

TABLE IV.—EQUIVALENT CONDUCTANCE AS A FUNCTION OF TEMPERATURE

$t°$, C.	Λ_{KCl} 0.01 N	Λ_{HNO_3} 0.01 N	Λ_{0,NH_4OH}	$\Lambda_{0,HOAc}$
0	77.28	253	157	
18	122.18	364	238	350
25	141.18	406	271	391
50	215.1	547	404	
75	295.0	675	525	
100	376.6	785	646	772
128	465.5	891		
156	560	976	907	979
218	742	...	1,140	1,163
306	910	...	1,404	1,266

TABLE V.—EQUIVALENT CONDUCTANCE AS A FUNCTION OF PRESSURE.

$\Lambda/\Lambda_{P=0}$

Press., kg./cm.²	HCl	LiCl	NaCl	KCl	RbCl	CsCl
			30°C.			
1	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
500	1.0256	1.0135	1.0078	1.0098	1.0076	1.0050
1,000	1.0464	1.0256	1.0100	1.0100	1.0042	1.0002
1,500	1.0616	1.0240	1.0016	1.0039	0.9980	0.9904
2,000	1.0715	1.0202	0.9924	0.9945	0.9850	0.9730
2,500	1.0775	1.0070	......	0.9775	......	0.9544
3,000	1.0812	0.9915	0.9545	0.9582	0.9493	0.9304
4,000	1.0828	0.9520	0.9100	0.9150	0.9002	0.8794
5,000	1.0780	0.9078	0.8618	0.8660	0.8517	0.8250
6,000	1.0682	0.8601	0.8126	0.8178	0.7995	0.7725
7,000	1.0545	0.8062	0.7578	0.7630	0.7478	0.7184
8,000	1.0392	0.7545	0.7075	0.7129	0.6966	0.6654
9,000	1.0218	0.7060	0.6598	0.6646	0.6474	0.6175
-0,000	1.0055	0.6600	0.6146	0.6168	0.5995	0.5705
			75°C.			
1	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
500	1.0125	0.9886	0.9875	0.9878	0.9870	0.9855
1,000	1.0190	0.9815	0.9720	0.9755	0.9690	0.9678
1,500	1.0218	0.9664	0.9570	0.9578	0.9530	0.9450
2,000	1.0218	0.9514	0.9472	0.9418	0.9342	0.9258
2,500	1.0225	......	......	0.9245	......	0.9024
3,000	1.0229	0.9218	0.9018	0.9047	0.8952	0.8820
4,000	1.0225	0.8845	0.8629	0.8670	0.8554	0.8378
5,000	1.0171	0.8468	0.8238	0.8275	0.8121	0.7955
6,000	1.0115	0.8120	0.7844	0.7900	0.7729	0.7537
7,000	1.0040	0.7755	0.7472	0.7525	0.7317	0.7125
8,000	0.9947	0.7400	0.7102	0.7150	0.6940	0.6720
9,000	0.9866	0.7067	0.6764	0.6785	0.6575	0.6340
10,000	0.9780	0.6722	0.6422	0.6445	0.6220	0.5980
11,000	0.9680	0.6418	0.6097	0.6098	0.5900	0.5650

In addition to being a function of the concentration and dielectric constant, the equivalent conductances are also functions of the temperature and pressure. Table IV gives the equivalent conductance of the strong electrolytes, potassium chloride and nitric acid, at 0.01 N and the equivalent conductance

of the weak electrolytes ammonium hydroxide and acetic acid at zero concentration over a considerable temperature range. The conductance of these electrolytes increases with increase of temperature, but the rate of increase in the case of the acids is not so great as the rate of increase in the case of the ammonium hydroxide solutions. The rate of increase of conductance with increase of temperature is greatest of all in the case of the potassium chloride solutions.*

The variation of the equivalent conductance with change of pressure is also marked. Table V includes comprehensive data obtained by Zisman† for some monovalent salts at two temperatures and at a solute concentration of 0.01 *N*.

The surprising fact shown by Table V is that the equivalent conductance increases with increase of pressure at the lower values of the pressure. In the case of hydrochloric acid the equivalent conductance at 30°C. at the high pressures is always greater than at atmospheric pressure. As the atomic weight of the cation gets larger, however, the equivalent conductance increases less with rise of pressure and in the case of cesium chloride the maximum in the conductance-pressure curve occurs at the low pressure of 500 kg. per square centimeter. At 75°C. there is no maximum except in the case of hydrochloric acid. The explanations underlying these interesting phenomena will be considered after the equivalent conductance of strong electrolytes as a function of concentration has just been studied. In the meantime we shall devote our attention to theories of conductance of weak electrolytes.

The Arrhenius Interpretation of the Equivalent Conductance Variation with Concentration.—Arrhenius attributed the decline in the equivalent conductance as the concentration increases to the decline in the number of ions per equivalent present in the solution. It was the ion which carried the current through the solution and the decrease in the conducting power of the solution was, therefore, explained on the assumption of a decrease in the number of ions per equivalent available for carrying the current. By referring to Eq. (18) which contains the constant F and the variables α, u, and v it is clear that a change in the

* Data from the "International Critical Tables."

† W. A. Zisman, *Phys. Rev.*, **39**, 151–160 (1932).

equivalent conductance might be due either to a change in α or a change in u and v. The classical Arrhenius theory assumes as a first approximation that the decrease of equivalent conductance with increasing concentration is due to a decrease in α and that u and v remain constant as the concentration increases. The application of Le Chatelier's principle to the equilibrium

$$AB \rightleftarrows A^+ + B^- \tag{21}$$

demonstrates that the dissociation of AB will be decreased with increase of concentration or conversely that the dissociation of AB will be increased with dilution. Arrhenius states that α will be equal to unity at zero concentration because the dissociation will be complete. If this is true, Eq. (18) becomes at zero concentration

$$\Lambda_0 = F(u_0 + v_0). \tag{22}$$

Dividing Eq. (18) by Eq. (22) and canceling $(u + v)$ with $(u_0 + v_0)$ since they are equal by our assumption above, we obtain an expression for α in terms of the equivalent conductance,

$$\frac{\Lambda}{\Lambda_0} = \alpha. \tag{23}$$

In Chap. II we derived the mass action law equation

$$K_c = \frac{\alpha^2 c}{1 - \alpha}. \tag{II-4}$$

Following Ostwald we may now introduce into this equation the value for α given by Eq. (23), obtaining

$$K_c = \frac{(\Lambda/\Lambda_0)^2 c}{1 - \dfrac{\Lambda}{\Lambda_0}},$$

or on rearrangement

$$\Lambda c = \frac{1}{\Lambda}\Lambda_0^2 K_c - \Lambda_0 K_c. \tag{24}$$

Equation (24) is known as *Ostwald's dilution law* and may readily be tested by plotting Λc against $1/\Lambda$; a straight line should result if the data agree with the Arrhenius theory. Figures 2 and 3 illustrate the agreement that is obtained in the case of a typical strong electrolyte, potassium chloride, and a typical weak

electrolyte, acetic acid. The acetic acid curve leaves nothing to be desired, but the curve for potassium chloride indicates that in the case of strong electrolytes there is a serious disagreement between theory and fact. In the next chapter we shall describe a theory which gives a more quantitative explanation of the conductances of strong electrolytes than does the Arrhenius theory.

The Arrhenius theory may also be tested graphically in another way in the case of solutions of such weak electrolytes that α is small in comparison to unity. Setting $1 - \alpha$ equal to unity in Eq. (II-4), we obtain the equation,

$$K_c = \alpha^2 c, \tag{25}$$

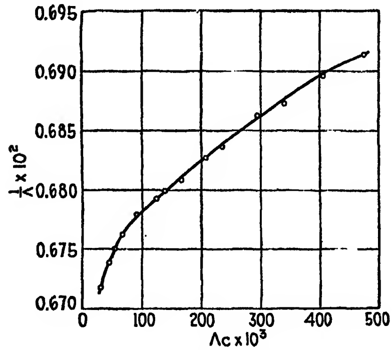

Fig. 2.—Potassium chloride at 25°.

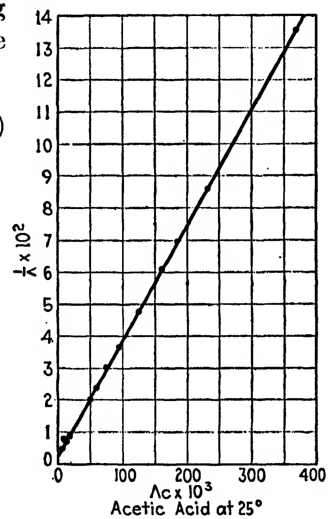

Fig. 3.—Acetic acid at 25°.

or, after substitution of α by Λ/Λ_0

$$\Lambda = \Lambda_0 \sqrt{K_c}\, c^{-\frac{1}{2}}. \tag{26}$$

Taking logarithms of Eq. (26),

$$\log \Lambda = \log \Lambda_0 \sqrt{K_c} - \tfrac{1}{2} \log c. \tag{27}$$

By plotting $\log \Lambda$ against $\log c$ a straight line should result having a slope equal to $-\frac{1}{2}$ if the Arrhenius theory is correct and if α may be neglected in comparison to unity. The experimental data of Kraus and Fuoss given in Fig. 1 are plotted according to this scheme; the short straight lines at the left of the drawing have the theoretical slope of -0.5. It is interesting to note

that the log Λ, log c curves of the weak electrolytes are nearly all parallel to the theoretical straight lines at the low concentrations, thus indicating in these cases that the conductance is determined by dissociation according to the law of mass action. The curves for the strong electrolytes give no indication of attaining a slope of -0.5 even at the lowest concentrations. Here, again, it is evident that the classical dissociation theory of Arrhenius receives splendid confirmation in the case of weak electrolytes, but fails to account satisfactorily for the conductance of strong electrolytes.

Fuoss and Kraus* have been successful in explaining the conductance minimum and the increase in equivalent conductance with increase in concentration illustrated by their data of Fig. 1. They have made use of the concept of *triple ions*, ions of the type $(+\ -\ +)$ or $(-\ +\ -)$, and have shown how the Arrhenius concept of partial dissociation can be applied to the equilibria involving these complex ions. They first point out, however, that calculations of the energy of dissociation of these triple ions on the basis of Coulomb's law indicate that in solvents of sufficiently low dielectric constant the triple ions will be stable (see Chap. II). Fuoss and Kraus assume that the following equilibria exist:

$$AB \rightleftarrows A^+ + B^- \tag{28a}$$

$$AB_2^- \rightleftarrows AB + B^- \tag{28b}$$

$$A_2B^+ \rightleftarrows AB + A^+. \tag{28c}$$

From the first equilibrium we have

$$\alpha_1 = \sqrt{K_1}c^{-1/2}, \tag{29a}$$

and from Eqs. (28*b*) and (28*c*),

$$\alpha_2 = \frac{c\alpha_1}{K_2}, \tag{29b}$$

and

$$\alpha_3 = \frac{c\alpha_1}{K_3}. \tag{29c}$$

K_2 and K_3 are the mass action constants for equilibria (28*b*) and (28*c*) and α_2 and α_3 are defined by the equations

$$\alpha_2 = \frac{c_{AB_2^-}}{c} \tag{30a}$$

* R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 2387 (1933).

and

$$\alpha_3 = \frac{c_{A_2B^+}}{c}. \tag{30b}$$

In the derivation of these equations Fuoss and Kraus make the justifiable assumption that c_{AB} equals the stoichiometrical concentration, c. By reasoning similar to that which we used in deriving Eq. (23) Fuoss and Kraus obtain the equation

$$\Lambda = \alpha_1\Lambda_{0,1} + \alpha_2\Lambda_{0,2} + \alpha_3\Lambda_{0,3}. \tag{31)*$$

Substituting Eqs. (29a) (29b), and (29c) for α_1, α_2, and α_3 into Eq. (31), the equation

$$\Lambda = \Lambda_{0,1}\sqrt{K_1}c^{-\frac{1}{2}} + \Lambda_{0,2}\frac{\sqrt{K_1}}{K_2}c^{\frac{1}{2}} + \Lambda_{0,3}\frac{\sqrt{K_1}}{K_3}c^{\frac{1}{2}},$$

or

$$\Lambda = k_1c^{-\frac{1}{2}} + k_2c^{\frac{1}{2}}, \tag{32}$$

where k_1 and k_2 are constants, results. Equation (32) predicts that the equivalent conductance will pass through a minimum at a certain concentration and thereafter increase as the concentration increases. Figure 4 illustrates graphically the triple-ion theory of Fuoss and Kraus. Curve 1 represents that part of the equivalent conductance which they calculate is due to the simple nitrate and tetraisoamylammonium ions. This conductance is directly proportional to $c^{-\frac{1}{2}}$ by Eq. (32). Curve 2 represents the equivalent conductance due to the triple ions; and by Eq. (32) this conductance is directly proportional to $c^{\frac{1}{2}}$. Curve 3 is the total equivalent conductance calculated by Eq. (32) and agrees satisfactorily with the experimental data which are represented by circles in Fig. 4.

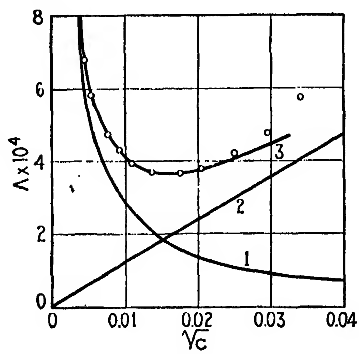

FIG. 4.

* The constants $\Lambda_{0,2}$ and $\Lambda_{0,3}$ are equal to Fv_2 and Fu_3, respectively. It must be remembered that this treatment is only valid for solutions in which α_1, α_2, and α_3 are small in comparison with unity. From the definitions of α_1, α_2, and α_3 it is evident that α_1 will be equal to unity at zero concentration, but α_2 and α_3 can never be equal to unity.

Fuoss and Kraus calculate that the triple ions formed from tetraisoamylammonium nitrate are unstable in solvents having a dielectric constant greater than 23.2; a minimum in the conductance-concentration curve cannot be found at any concentration in dioxane-water mixtures of greater dielectric constant than this.

Further verification of the assumptions of Fuoss and Kraus concerning the existence of triple ions and other complex aggregates is found in the work of Kraus and Vingee, *J. Am. Chem. Soc.*, **56**, 511 (1934), who have determined the molecular weight of tetraisoamylammonium nitrate in dioxane by the lowering of the freezing-point method. At $4 \times 10^{-3} N$ the molecular weight is approximately twice the formula weight and increases with increasing concentration.

With the exception of strong electrolytes, the Arrhenius interpretation of the variation of the equivalent conductance with concentration may be considered to be substantially correct, although it may be necessary to expand Arrhenius's theory in the future to account for unexplainable data as Fuoss and Kraus have done in their triple-ion theory.

Equivalent Conductance, the Degree of Dissociation, and the Dissociation Constant.—In the last section we have been content to examine the Arrhenius theory solely to test its agreement with the data and have said nothing concerning the actual calculation of the degree of dissociation α and the dissociation constant K. It is obvious from Eq. (23) that to calculate α the equivalent conductance at zero concentration, Λ_0, must be known. Of course it is impossible to measure this quantity experimentally; it must be determined by calculations involving extrapolation of the experimental data to zero concentration. By examining the equivalent conductance values for the weak electrolyte, acetic acid, given in Table I it is evident that even at the lowest concentrations at which it is possible to make measurements the equivalent conductance is only about 50 per cent of its value at zero concentration. The extrapolation of the data in the case of acetic acid is for this reason quite impossible; recourse must be had to indirect methods of obtaining the limiting conductance. For strong electrolytes the situation is far more favorable inasmuch as the equivalent conductance measured at the lowest concentration possible is practically equal to the value at zero

concentration; thus Shedlovsky* in his accurate work on the conductance of strong aqueous electrolytes finds that the equivalent conductance of hydrochloric acid at $0.00002841c$ is 425.01, whereas the value at zero concentration is found by extrapolation to be 426.04. The uncertainty in this small extrapolation cannot be serious. Kohlrausch discovered that the conductances of strong electrolytes in very dilute solution agreed with the "square-root law," a relationship suitable for extrapolation and one which has been given a theoretical significance by Debye and Hückel as we shall see in the next chapter.

The limiting conductance of weak electrolytes can be calculated, however, quite accurately by a method based on Kohlrausch's *law of independent migration of ions.*†

Kohlrausch discovered that differences between Λ_0 for salts containing a common ion were constant and independent of the common ion. The difference between Λ_0 for potassium chloride and sodium chloride at 18° is 21.1 while the difference between Λ_0 for potassium nitrate and sodium nitrate is also 21.1. Some data obtained by Kohlrausch to prove his law are given in Table VI. Assuming the correctness of Kohlrausch's law about

TABLE VI.—THE KOHLRAUSCH LAW OF THE INDEPENDENT MIGRATION OF IONS

Salt	Λ_0	Salt	Λ_0	Difference K − Na
KCl	130.0	NaCl	108.9	21.1
KNO_3	126.3	$NaNO_3$	105.2	21.1
K_2SO_4	133.0	Na_2SO_4	111.9	21.1

which we have no doubts, we can obtain the limiting conductance of the weak electrolyte, acetic acid, from the equation

$$\Lambda_{0,\mathrm{HOAc}} = \Lambda_{0,\mathrm{HCl}} + \Lambda_{0,\mathrm{NaOAc}} - \Lambda_{0,\mathrm{NaCl}}. \tag{33}$$

Since hydrochloric acid, sodium acetate, and sodium chloride are all strong electrolytes, there is not much uncertainty in regard to the Λ_0 value for these substances and correspondingly not much uncertainty in regard to Λ_0 for acetic acid.

In the case of solutions in solvents of lower dielectric constant the situation is not so simple owing to the fact that there are

* T. SHEDLOVSKY, *J. Am. Chem. Soc.*, **54**, 1411 (1932).

† KOHLRAUSCH, *Wied. Ann.*, **6**, 1 (1879); **26**, 161 (1885).

no strong electrolytes in these solvents. The limiting conductance must be evaluated for a given electrolyte from conductance data relating to that electrolyte alone. Fuoss and Kraus* have recently invented an excellent method of determining Λ_0; the reader is referred to their paper for complete details.

The calculation of the degree of dissociation from Eq. (23) follows very easily when Λ_0 has been determined. As a matter of fact we now know that Arrhenius's assumption that $(u_0 + v_0)$ equals $(u + v)$ is not quite correct due to the fact that the mobilities of the ions change with changing concentration. The proper method of calculating α was first pointed out by Davies† and later independently by Sherrill and Noyes‡ and by MacInnes.§ The new method consists in calculating α from the equation

$$\alpha = \frac{\Lambda(u_0 + v_0)}{\Lambda_0(u + v)},$$

or more simply,

$$\alpha = \frac{\Lambda}{\Lambda_e}, \tag{34}$$

where

$$\Lambda_e = \Lambda_0 \frac{(u + v)}{(u_0 + v_0)}. \tag{35}$$

The principles underlying the calculation of Λ_e will be given in the next chapter; here we shall be content to quote actual data for acetic acid recently published by MacInnes and Shedlovsky.‖ In Table VII, the dissociation constant K_c calculated from the equation,

$$K_c = \frac{c\alpha^2}{1 - \alpha} \tag{II-4}$$

is not so constant with change of concentration as the values for K for acetic acid given in Table I of Chap. II.

* Fuoss and Kraus, *J. Am. Chem. Soc.*, **55**, 476 (1933); **57**, 488 (1935).

† C. Davies, *J. Phys. Chem.*, **29**, 977 (1925).

‡ M. S. Sherrill and A. A. Noyes, *ibid.*, **48**, 1861 (1926).

§ D. A. MacInnes, *J. Am. Chem. Soc.*, **48**, 2068 (1926).

‖ D. A. MacInnes and T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1429 (1932).

TABLE VII.—CONDUCTANCE AND DISSOCIATION DATA FOR ACETIC ACID

Concn. $c \times 10^3$	Λ	Λ_e	α	$K_c \times 10^5$
0.028014	210.32	390.02	0.5393	1.768
0.11135	127.71	389.68	0.3277	1.779
0.15321	112.02	389.61	0.2875	1.777
0.21844	96.466	389.49	0.2477	1.781
1.02831	48.133	388.94	0.1238	1.797
1.36340	42.215	388.81	0.1086	1.803
2.41400	32.208	388.52	0.08290	1.809
3.44065	27.191	388.32	0.07002	1.814
5.91153	20.956	387.99	0.05401	1.823
9.8421	16.367	387.61	0.04223	1.832
12.829	14.371	387.41	0.03710	1.834
20.000	11.563	387.05	0.02987	1.840
50.000	7.356	386.19	0.01905	1.849
52.303	7.200	386.07	0.01865	1.854
100.000	5.200	385.29	0.01350	1.846
119.447	4.759	385.07	0.01236	1.847
200.000	3.650	384.41	0.009495	1.821
230.785	3.391	384.15	0.008827	1.814

$\Lambda_0 = 390.59$

We still need to apply one more correction to our method of calculating K, a correction which we shall describe after the Lewis activity coefficient concept has been introduced into the book.

The figures for α in Table VII are quite correct, at least in the dilute solution range of concentration, and may be considered as being the correct measure of the number of ions present. It is to be regretted that we do not know α for all electrolytes with the same accuracy that we know α for acetic acid. Only in the case of weak electrolytes can we calculate α and in this way be reasonably certain of the number of ions present in a cubic centimeter of solution.

The dissociation constant K is an important quantity inasmuch as it is a measure of the chemical "strength" of acids and bases. In the chapter on homogeneous equilibria we shall go more fully into the importance and usefulness of K; in this chapter where we are attempting to interpret the experimental values of the equivalent conductance we shall limit our discussion of K to the variation of K with dielectric constant, temperature and pressure.

The Dissociation Constant as a Function of the Dielectric Constant.—In Chap. II, Table VI, are given some experimental values of the dissociation constant of tetraisoamylammonium nitrate in mixtures of dioxane and water as a function of the dielectric constant. The dissociation constant varies from 2×10^{-16} to 0.25 as the dielectric constant varies from 2.38 to 38.0. The underlying ideas of the theoretical explanation of the dissociation constant in terms of Coulomb's law have already been discussed in Chap. II; it will be remembered that the dissociation of a salt depends upon the energy with which the ions are bound together and the energy of binding depends upon the dielectric constant of the medium. In this way the dissociation constant may be related to the dielectric constant of the solvent and may be calculated in terms of the dielectric constant, temperature, and size of the ions. This calculation is quite involved, but has been carried out by Fuoss and Kraus* for solutions of tetraisoamylammonium nitrate in dioxane-water mixtures. In Fig. 5 the calculated values of the dissociation constant as a function of the dielectric constant are represented by the solid line while the experimental data are represented by solid circles. It is interesting to note that log K tends to approach infinity at a value of the dielectric constant equal to 43.6. An infinite value of K could be produced by *complete dissociation* since in this case $1 - \alpha$ becomes zero and K is equal to $\alpha^2 c/0$ or infinity.

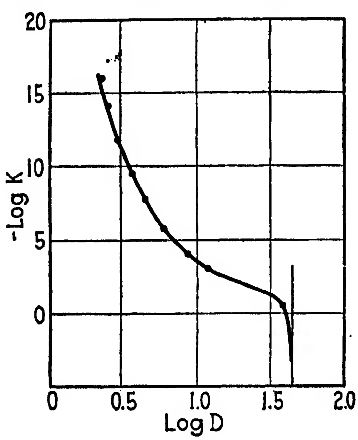

Fig. 5.

The results of Fuoss and Kraus are important in that they indicate that the mass action equilibrium for the dissociation is primarily controlled by Coulomb forces between the ions, at least for these particular solutions. It must be kept in mind, however, that the dissociation constants of most substances have not yet been theoretically calculated.

* R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 1019 (1933).

The Dissociation Constant as a Function of Temperature and Pressure.—The dissociation constants of the weak electrolytes acetic acid and ammonium hydroxide as a function of temperature are given in Table VIII.

TABLE VIII.—DISSOCIATION CONSTANTS AS A FUNCTION OF TEMPERATURE[a]

$t°$, C.	$K_{c_{NH_4OH}}$	$K_{c_{HOAc}}$
0	1.39×10^{-5}	
18	1.72×10^{-5}	1.81×10^{-5}
25	1.81×10^{-5}	1.81×10^{-5}
40	1.98×10^{-5}	
50	1.81×10^{-5}	
75	1.64×10^{-5}	
100	1.35×10^{-5}	1.1×10^{-5}
156	6.28×10^{-6}	5.3×10^{-6}
218	1.80×10^{-6}	1.7×10^{-6}
306	9.3×10^{-8}	1.4×10^{-7}

[a] Data from the "International Critical Tables."

One would expect on the basis of kinetic considerations alone that the dissociation of a substance would rise with increasing temperature. Above 40°C. this is not true, the dissociation decreases with rise of temperature. Kraus* points out that due to the decreasing value of the dielectric constant of water with increasing temperature, aqueous electrolytes tend to approach nonaqueous electrolytes in their behavior. At 100°C. the dielectric constant of water† has fallen to 44 and it is still lower at higher temperatures. Possibly a decrease in the size of ions at higher temperatures may affect the dissociation constant although nothing definite is known concerning this point.

Fuoss‡ has derived an explicit expression for $\frac{1}{\Lambda}\frac{d\Lambda}{dT}$ for weakly dissociated electrolytes, particularly for binary electrolytes in

* C. A. KRAUS, "The Properties of Electrically Conducting Systems," p. 152, Chemical Catalog Company, Inc., New York, 1922.

† The "International Critical Tables" give the following equation for the dielectric constant of water as a function of temperature,

$$D \doteq 80 - 0.4(t - 20°),$$

where D and t are the dielectric constant and degrees centigrade, respectively.

‡ R. M. FUOSS, *J. Am. Chem. Soc.*, **56,** 1857 (1934).

solvents of dielectric constant under 10, by differentiating Eq. (32) with respect to the temperature. The temperature coefficient of the conductance is shown to depend primarily on the temperature coefficient of the viscosity of the solvent (see Chap. VI), and secondarily on the change of the dielectric constant with change of temperature. Bien, Kraus, and Fuoss* have tested the equations of Fuoss with data for tetrabutylammonium nitrate and picrate in anisole. The results seem to conform to their ideas concerning the existence of triple ions. They assume that the ion size is independent of temperature.

According to the principle of Le Chatelier the effect of pressure on dissociation should depend upon the difference in volume between the ions and the undissociated molecules. If the total volume of the ions is less than that of the undissociated molecule, increase of pressure should increase the extent of dissociation. With weak electrolytes increase of pressure increases the electrical conductance of the solutions to a greater extent than it does strong electrolytes.† The explanation of increased conductance is probably to be found in an increase of dissociation with increase of pressure. The dielectric constant of water increases with increasing pressure; this increase of dielectric constant should promote a greater dissociation.‡

Exercises

1. Test the Ostwald dilution law graphically using the data for formic and cyanoacetic acids in Table III.
2. Test the relation $\log \Lambda \sim \log c$ graphically using the data for acetic and cyanoacetic acids in Table III. Compare the slope of the lines with the theoretical slope.
3. Derive Eq. (31).
4. Calculate the dissociation constant for 0.01 and 0.003c lanthanum chloride using the Eq. (II-4).

* Bien, Kraus, and Fuoss, *J. Am. Chem. Soc.*, **56**, 1860 (1934).

† See Kraus, *loc. cit.*, p. 136.

‡ The "International Critical Tables" gives the following equation for the dielectric constant of water as a function of pressure at a temperature of 16.3°C.:

$$D = 81.5(1 + 46 \times 10^{-6}P),$$

where P is the pressure in atmospheres.

CHAPTER VI

THEORETICAL INTERPRETATION OF THE CONDUCTANCE OF ELECTROLYTES

II. THE INTERIONIC ATTRACTION THEORY

The Anomaly of Strong Electrolytes.—In the last chapter we have seen that highly conducting or strong electrolytes fail to verify the Ostwald dilution law or the law of mass action. In the early days of the Arrhenius theory many attempts were made to modify the Ostwald dilution law by the introduction of empirical constants, but the equations obtained, although agreeing with the data in many cases, failed to give a better understanding of the true nature of strong electrolytes. It was thought by some that the mass action law would be obeyed by strong electrolytes in the region of extremely dilute solutions. However, this did not turn out to be the case when experimental technique made possible the investigation of the extremely dilute solutions.

In addition to the failure of strong electrolytes to agree with the mass action law there were other difficulties. It will be remembered that the Arrhenius calculation of the degree of dissociation assumed that the mobility of an ion at any finite concentration was equal to its mobility at zero concentration. Although it is impossible to measure directly the mobility of a *single* ion kind, the determination of the *ratio* of the mobility of the positive ion to that of the negative ion can be carried out by means of transference number measurements (to be described in a later chapter). These ratios were found to change with changing concentration; thus indicating that the mobilities of the ions were not constant. Attempts to explain these changing ratios on the basis of a change in the hydration of ions were not satisfactory in that no quantitative test of this hydration theory was possible.

Other serious difficulties offered by strong electrolytes to the simple Arrhenius theory were the calculation of different values of the degree of dissociation depending upon the method used and the calculation of degrees of dissociation greater than unity.

It was discovered that the degree of dissociation calculated from e.m.f. data of strong electrolytes and from conductance data did not agree with each other. In concentrated solutions the difference was marked. Furthermore, the degree of dissociation calculated from e.m.f. data of hydrochloric acid solutions, for example, was over 2 at 5 *N*. A dissociation of 200 per cent obviously has no physical significance.

Perhaps the strongest criticism of the unmodified Arrhenius theory is that it failed to consider the electric attractions that must exist between ions of unlike sign when dissolved in solution.

We know from Coulomb's law that the force of attraction between two charged bodies at distance r apart and in a medium of dielectric constant D is

$$f = \frac{q_1 q_2}{Dr^2}. \tag{1}$$

There is no reason for believing that there should be no "Coulomb forces" between the ions in any solution. If ions exist, the electrical forces must exist also. The first person to realize this was J. J. van Laar,* but his ideas did not arouse the interest of scientists, probably as they came before the wealth of experimental evidence had been built up showing the inadequacy of the simple Arrhenius theory for strong electrolytes. In 1907 Sutherland† pointed out that the change of equivalent conductance of electrolytes with change of concentration was due to an electric rigidity in the solutions and that dissociation was complete in all ordinary solutions. The electric rigidity of the solutions or the tendency of the ions in the solution to take on a space lattice arrangement was due to the electrostatic interionic forces which changed with the concentration. However, Sutherland's mathematical development failed to impress.

The interionic attraction point of view was emphasized by Bjerrum‡ in 1909 and, no doubt, had considerable influence upon scientists. Milner§ was the first to calculate theoretically the

* J. J. van Laar, *Z. physik. Chem.*, **18**, 273 (1895); *Archives Teyler* (2) **7**, 1st part, pp. 1–37 (1900).

† W. Sutherland, *Phil. Mag.*, (6) **14**, 3 (1907).

‡ N. Bjerrum, *Proceedings of the 7th International Congress of Applied Chemistry*, London, May 27, 1909. Section X, "A New Form for the Electrolytic Dissociation Theory."

§ Milner, *Phil. Mag.*, **23**, 551 (1912); **25**, 742 (1913).

effect of the electrostatic interionic attractions on thermodynamic functions; he did not deal with the theoretical interpretation of conductance values, and his mathematical treatment was of such a nature as to prevent a complete solution of the problem. Ghosh* calculated the variation of conductance with concentration from a mathematical basis, the equivalent conductance change (at very low concentrations) being proportional to the cube root of the concentration. Unfortunately Ghosh had to assume a stationary distribution of ions throughout the solution in order to calculate the potential due to the electric field of the ions in the medium, and as we know that the ions must be endowed with a certain kinetic energy, *i.e.*, they must be continually in motion, Ghosh's treatment is invalid on a physical basis. Ghosh's final equation, furthermore, did not agree with the data. However, his work was important; for Debye, in his attempt to improve Ghosh's theoretical treatment, was led to the interionic attraction theory that bears his name. This theory has now been verified for a number of unrelated phenomena of strong electrolytes in dilute aqueous solution and has had a considerable influence not only in modifying our ideas of electrolytes but also in stimulating and suggesting further researches.

The Debye Theory of Solutions.—In developing their mathematical theory of electrolytes, Debye and Hückel† made use of the following fundamental ideas: It is assumed that electric forces of attraction and repulsion exist between ions which may be calculated in accordance with Coulomb's law. Because of these forces a perfectly random distribution of the ions is impossible, but due to the attractions that exist between ions of unlike sign there will be more ions of unlike sign in the neighborhood of an ion than there are ions of like sign. Thus a positive ion will be surrounded by more negative ions than positive ions, and a negative ion will be surrounded by more positive ions than negative ions. In the stationary case‡ the ions tend to build up

* Ghosh, *J. Chem. Soc.*, **113**, 449, 627, 707, 790 (1918).

† P. Debye and E. Hückel, *Physik. Z.*, **24**, 185, 305 (1923); see also the following reviews: J. W. Williams and H. Falkenhagen, *Chem. Rev.*, **6**, 317 (1929); H. Falkenhagen, *Rev. Modern Phys.*, **3**, 412 (1931).

‡ The stationary case is defined as the case in which the ions are subject solely to internal forces such as thermal forces and electrical forces due to other ions. Nonstationary situations exist when the ions are subject to an

a symmetrical distribution, but this tendency is opposed by the Brownian motion of the ions so that we can say that on the time average there are more ions of unlike sign in the neighborhood of an ion than there are ions of like sign. The particular distribution of ions about a certain ion is called the "ionic atmosphere," and is of such a nature that it gives a potential in the place of the ion of opposite sign to the ion in question. But if the ionic atmosphere about an ion were always perfectly symmetrical, the interionic attractions would not affect the velocity of the ion under an applied electric field, because the motion of the ion would be hindered by the ions behind it just as much as it is helped by the ions before it, and there would be no net effect on the ion. However, the ionic atmosphere about an ion moving in a definite direction is not symmetrical due to a factor called the *time of relaxation* of the ionic atmosphere. If the ionic atmosphere had a zero time of relaxation, it would mean that the ions in the solution could move from a perfectly haphazard and random distribution to their symmetrical arrangement in zero time. But it takes a definite duration of time for the symmetrical ionic atmosphere to be built up; hence as the ion moves through the solution in the x-direction, let us say, the distribution in front of the ion at the position $x + dx$ has not had time to build itself up to its maximum value, and the distribution in back of the ion at the position $x - dx$ has not had the time to fall away to its minimum value. This results in the retarding forces behind the ion being greater than the accelerating forces ahead of the ion, so that the ion moves against a net retarding force due to the unsymmetrical (but not random) distribution of the ions about it. The greater the velocity of the ion due to the electric field, the greater the asymmetry of the atmosphere and the greater the retarding force due to this effect; at constant velocity of the ion the retarding force is constant. It will be realized from this discussion, perhaps, that the time of relaxation is necessarily a function of the mobilities of the ions; a swiftly moving ion like the hydrogen ion can help to build up the atmosphere more quickly than a slowly moving ion. This accounts for the interesting mathematical deduction

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applied electric field of any kind or to a shearing motion such as occurs in viscous flow.

that the interionic effects in the nonstationary cases are dependent among other things upon the mobilities of the ions. The times of relaxation, as given by Williams and Falkenhagen, for some electrolytes at a concentration of 0.001c are tabulated in Table I.

TABLE I

Electrolyte	Time of Relaxation at 18°, Sec.
KCl	0.553×10^{-7}
HCl	0.189×10^{-7}
$MgCl_2$	0.324×10^{-7}
$CdSO_4$	0.315×10^{-7}
$LaCl_3$	0.162×10^{-7}

The time of relaxation is also a function of the concentration of the *ions*, as are the nature and extent of the ionic atmosphere. At zero concentration, the radius of the ionic atmosphere is infinite since the ions are an infinite distance apart; with increasing concentration, the thickness of the ionic atmosphere about an ion decreases, so that the position of maximum density of the ionic atmosphere may be considered as getting closer to the ion as the concentration increases. Just as the radius of the ionic atmosphere gets smaller as the concentration increases, the period of time necessary to build it up gets smaller. At zero concentration the time of relaxation is infinite; the ions being an infinite distance apart, it would take an infinite time to bring them into a symmetrical distribution.

Now Debye and Hückel realized that to calculate the electrical retarding forces on an ion due to the other ions in solution, it was necessary to know the concentration of the ions. On account of the inapplicability of the Ostwald dilution law to strong electrolytes, there was no definite means of ascertaining the number of ions in a solution of a salt such as potassium chloride. Hence Debye and Hückel made the assumption that strong electrolytes were completely dissociated in order to calculate the effect of interionic attractions. The conclusions of Fuoss and Kraus concerning the dissociation of the strong electrolyte tetraisoamylammonium nitrate in water published 10 years after the original papers of Debye and Hückel* lend considerable support to the assumption of complete dissociation. Because

* R. M. FUOSS and C. A. KRAUS, *J. Am. Chem. Soc.*, **55**, 1019 (1933). See Chaps. II and V.

Debye and Hückel made this assumption their theory is sometimes called the *theory of complete dissociation*. This title is erroneous, however, because the Debye treatment is equally applicable to the case of a weak electrolyte like acetic acid. In the case of acetic acid Ostwald's dilution law applies, and it is possible to calculate the ionic concentration. It is the ionic concentration that Debye is interested in, and it is this concentration that is used to calculate the effect of the interionic forces on conductance, etc.

In the development of the conductance theory, Debye and Hückel postulate that the decrease in the molal conductance of strong electrolytes as the concentration increases is due chiefly to a decrease in the mobilities of the ions rather than to a decrease in the extent of dissociation as postulated by Arrhenius, the decrease in mobilities being due, first, to the electrical retarding force, or the electric force of relaxation, of the asymmetric ionic atmosphere about the ion. There is also another retarding force called the *electrophoretic* effect which is explained in this way. Owing to its electrical charge and its polarizing effect on the solvent molecules each ion attracts to itself a certain amount of the solvent molecules and carries or tends to carry the solvent with it as it moves through the solution. Since a positive ion is surrounded on the average by negative ions and since the negative ions tend to move the solvent in a direction opposite to that of the positive ion, it is evident that the positive ion is moving through a solvent which itself is moving in the opposite direction. This effect results in an additional retarding force which is to be added to the frictional retarding force of the medium. To sum up all the forces that act on an ion we can write

Electrical forces = frictional forces,

or

outside applied electric force + electric force of relaxation
= frictional force of the medium +
frictional force of the electrophoretic effect.

In order to calculate these forces Debye and Hückel make use of the general equation of Brownian motion as derived by Einstein, introducing into the Einstein equation forces to allow for the electrical effects upon the ions. For the forces given above (in the order named) Debye and Hückel obtain

$$\epsilon z_i X - \frac{1}{6}\rho\frac{\bar{v}_i}{DkT}\kappa\epsilon^2 z_i^2 = \rho_i v_i + \epsilon z_i \kappa b_i X. \tag{2}$$

In Eq. (2) the symbols have the following significance:

ϵ = elementary charge of electricity.

z_i = valence of an ion.

X = applied electric field.

ρ = friction coefficient; from Stokes's law

$$\rho_i = 6\pi\eta b_i \qquad \text{and} \qquad \rho = \frac{\Sigma n_i q_i^2 \rho_i}{\Sigma n_i q_i^2}.$$

b_i = radius of ion or moving particle.

$\bar{v}_i$ = velocity of ion.

D = dielectric constant of the solvent.

k = gas constant for one molecule = $R/\mathbf{N}$ ($\mathbf{N}$ = Avogadro's number).

T = absolute temperature.

n_i = number of ions of one kind per cubic centimeter.

A very important quantity in the Debye theory is κ which contains among other things the concentration

$$\kappa = \sqrt{\frac{4\pi\epsilon^2\mathbf{N}}{1{,}000DkT}\Sigma\nu_i z_i^2}\sqrt{c}. \tag{3}$$

In Eq. (3) $\mathbf{N}$ is Avogadro's number and c is the concentration in moles per liter of solution. At constant temperature all the quantities under the first square-root sign are constant; hence κ is directly proportional to the square root of the concentration. Debye and Hückel simplified Eq. (2) to

$$\bar{\Lambda} = \bar{\Lambda}_0 - A'\sqrt{c}, \tag{4}$$

where A' is a constant. In other words Debye and Hückel have shown mathematically that $\bar{\Lambda}_0 - \bar{\Lambda}$ is directly proportional to the square root of the *ionic* concentration. Many years before, Kohlrausch had used a function similar to Eq. (4) for the purpose of extrapolating his conductance values to zero concentration. His empirical equation is known as the "Kohlrausch square-root law." Debye and Hückel were the first to give any theoretical significance to Kohlrausch's equation. Shedlovsky's* data for potassium chloride are plotted as a function of the square root

* T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1423 (1932).

of the concentration in Fig. 1, and it can be seen that the Debye or Kohlrausch relationship is verified. As the solutions become appreciably concentrated, however, the data no longer agree with the square-root law (data above 0.0032 N are not shown in the plot). Since this deviation at higher concentrations occurs with all electrolytes, we can make the general statement that the Debye equations are valid only for very low concentrations.

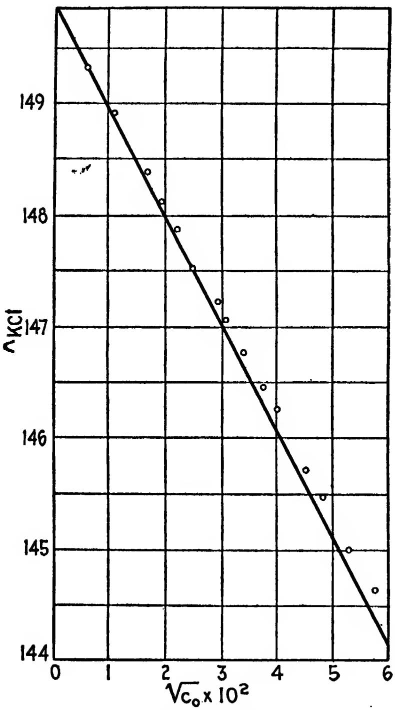

FIG. 1.—Equivalent conductance of potassium chloride as a function of the square root of the concentration.

A more rigid test of the Debye theory consists in comparing the theoretically calculated constant, A', with that experimentally observed. In the original work of Debye and Hückel the A' constant contained the radius of the ion, and since we possess no definite information concerning the sizes of ions in solution, Debye and Hückel were unable to calculate A' theoretically. Fortunately the mathematical calculations of Debye and Hückel have been extended and improved by Onsager in such a way that many difficulties and theoretical objections to the original treatment have been overcome and the equations extended so that the constant A' can be mathematically calculated provided the limiting conductance is known and thereby compared with the experimental values.

The Conductance Theory of Onsager.—In Onsager's* papers on the electrical conductance of solutions he first showed how the electrophoretic effect could be calculated without a knowledge of the ionic radius b_i; the result being

* L. ONSAGER, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927); L. ONSAGER and R. M. FUOSS, *J. Phys. Chem.*, **36**, 2689 (1932).

$$\text{Electrophoretic force} = \frac{\epsilon z X \kappa}{6\pi\eta}. \tag{5}$$

In his second paper Onsager pointed out that the assumption of Debye and Hückel that the ionic atmosphere about the ion, or the ion with its asymmetrical distribution of ions about it, moves through the solution in a straight line does not correspond to physical facts, but that if a constant force is applied, the ion will find its own way through the solution. The Brownian movement of the ion will have an effect upon the asymmetry of the ionic atmosphere, an effect neglected by Debye and Hückel. The net result will be that the retarding force on the ion will be less when calculated in accordance with Onsager's postulates. Onsager also improved the treatment of Debye and Hückel by allowing for the mutual effect of the relaxation of both ionic atmospheres on each other.

Onsager's mathematical treatment is long and involved and for this reason cannot be considered here. His final equation for the molal conductance is

$$\bar{\Lambda} = \bar{\Lambda}_0 - \left[\frac{0.986 \times 10^6}{(DT)^{3/2}} B\bar{\Lambda}_0 + 29.0\frac{\Sigma \nu_i z_i^2}{(DT)^{1/2}\eta}\right]\sqrt{\Sigma \nu_i z_i^2}\sqrt{c}, \tag{6}$$

where

$$B = \frac{2G}{1 + \sqrt{G}} z_1 z_2 \tag{7}$$

and

$$G = \frac{z_1 z_2 (u_1^0 + u_2^0)}{(z_1 + z_2)(z_2 u_1^0 + z_1 u_2^0)}. \tag{8}$$

Equation (6) is of the form

$$\bar{\Lambda} = \bar{\Lambda}_0 - A\sqrt{c},$$

which is of exactly the same form as the equation of Debye and Hückel [Eq. (4)], but in the case of Onsager's equation it is possible to calculate theoretically the numerical value of the constant A. For the equivalent conductance Λ of a uni-univalent electrolyte, Eq. (6) reduces to

$$\Lambda = \Lambda_0 - \left[\frac{5.78 \times 10^5 \Lambda_0}{(DT)^{3/2}} + \frac{58.0}{(DT)^{1/2}\eta}\right]\sqrt{2c}. \tag{9}$$

The most accurate and perhaps the only strictly reliable test of Eq. (6) has recently been carried out by Shedlovsky* who concludes that measurements of the equivalent conductances of aqueous solutions of sodium chloride, potassium chloride, hydrochloric acid, silver nitrate, and potassium nitrate at 25°C. confirm the Onsager conductance equation as a *limiting* equation. In Fig. 1 the solid line represents conductances theoretically

TABLE II.—TEST OF THE ONSAGER EQUATION FOR HCl

$\Lambda = 426.04 - 156.64\sqrt{c}$

c	$\sqrt{c}$	$\Lambda_{calcd.}$	$\Lambda_{obs.}$	Diff.
0.00002841	0.005330	425.21	425.01	−0.20
0.00008118	0.009010	424.63	424.75	0.12
0.00017743	0.01332	423.95	423.82	−0.13
0.00031863	0.01785	423.24	423.43	0.19
0.00034227	0.01850	423.14	423.22	0.08
0.00059146	0.02432	422.23	422.42	0.19
0.00075404	0.02746	421.74	421.66	−0.08
0.0015768	0.03971	419.82	419.88	0.06
0.0018766	0.04332	419.25	419.64	0.39
0.0025614	0.05061	418.11	418.32	0.21
0.0029943	0.05472	417.47	417.98	0.51

calculated by Onsager's equation, and in Table II are given some actual numerical data for hydrochloric acid in order to demonstrate the kind of agreement that can be obtained. The last column of the table shows that up to a concentration of 0.0016 c the maximum difference between the observed and calculated values, 0.20 is only 0.05 per cent. But above the very dilute concentration of 0.0016 c the theoretical values become gradually smaller than the experimental values as the concentration is raised.

There are many reasons for the failure of the Onsager equation to agree with the data above the dilute concentration range. Onsager himself states that his equation is to be considered solely as a limiting equation; that is, his equation predicts conductance values to which the actual data should approach more and more as the concentration is lowered. The data of Shedlovsky and

* T. SHEDLOVSKY, *J. Am. Chem. Soc.*, **54**, 1411 (1932).

also other data amply bear out Onsager's conclusion that his equation is applicable only in the most dilute solutions.

In his mathematical development, Onsager found it necessary to make approximations and to drop higher terms of series expansions; since these effects are of negligible magnitude solely in the region of very dilute solutions, the mathematical result should only be valid in very dilute solutions.

The inapplicability of the Onsager* equation to moderate or high concentrations does not necessarily mean that the fundamental postulate of the decrease in equivalent conductance due to the interionic attractions is no longer applicable. It may mean that the mathematical problems are too complex to solve at the present time.

An interesting consequence of the theory of Onsager is seen in the work of Longsworth† and of Bennewitz, Wagner, and Küchler‡ who have measured the ionic conductances of a third ion in the presence of two other ions. Longsworth's accurate data for the conductances of the chloride, hydrogen, and potassium ions in 0.1 N solutions are given in Table III.

The equivalent conductance of the hydrogen ion declines in value as the hydrogen ion is taken from a pure hydrochloric acid solution and placed in a pure potassium chloride solution, while that of the potassium ion increases in value as the potassium ion is taken from pure potassium chloride and placed in a pure hydrochloric acid solution. The conductance of the chloride ion varies much less.

Bennewitz, Wagner, and Küchler have worked out the theory of these experiments in accordance with the mathematical treat-

* Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932) point out that a mathematical extension of the conductance equation would yield terms proportional to c log c and c. See also Fuoss, *Physik. Z.*, **35**, 59 (1934). Shedlovsky and Brown, *J. Am. Chem. Soc.*, **56**, 1066 (1934), find that an equation of the form

$$\Lambda_0 = \frac{\Lambda + \beta\sqrt{c}}{1 - \alpha\sqrt{c}} - B(c) + D(c) \log c,$$

where α, β, B, and D are constants is necessary to reproduce conductance values for aqueous solutions of the alkaline earth chlorides. Shedlovsky, Brown and MacInnes have recently discussed this subject in *Trans. Am. Electrochem. Soc.*, Preprint 66-23, October (1934).

† L. G. Longsworth, *J. Am. Chem. Soc.*, **52**, 1897 (1930).

‡ Bennewitz, Wagner, and Küchler, *Physik. Z.*, **30**, 623 (1929).

TABLE III.—EQUIVALENT CONDUCTANCES OF THE HYDROGEN, POTASSIUM, AND CHLORIDE IONS IN MIXTURES OF POTASSIUM CHLORIDE AND HYDROCHLORIC ACID AT CONSTANT TOTAL CONCENTRATION OF 0.1 NORMAL AND AT 25°C.

c_{H}/c_{Cl}	Λ_{H}	Λ_{K}	Λ_{Cl}
1.00	324.96	65.5[a]	66.32
0.75	322.4	65.2	66.19
0.50	319.9	64.1	66.07
0.25	316.9	63.7	65.83
0.00	314.0[a]	63.14	65.75

[a] Extrapolated values.

ment of Onsager. Onsager's equation for the equivalent conductance of an ion is

$$\Lambda_i = \Lambda_i^0 - \left(\frac{0.986 \times 10^6}{(DT)^{3/2}} B\Lambda_i^0 + \frac{29.0}{\eta(DT)^{1/2}} z_i\right)\sqrt{(\Sigma z_i)N}. \quad (10)$$

Equation (10) predicts that for symmetrical salts* the ionic conductance will be independent of the co-ion. The conductance of the chloride ion should be the same in the potassium chloride solutions as it is in hydrochloric acid solutions if the Onsager theory is correct. The data of Table III bear out this prediction rather closely since the conductance of the chloride ion does not change much as the relative concentration of the hydrogen and potassium ion varies. But the conductance of a third ion present in small quantities in a solution of two other ions depends upon the mobilities of these two ions. The equation derived by Bennewitz, Wagner and Küchler† for the conductance of a third

* Symmetrical salts are defined here as those salts whose ions have equal valences; KCl, $MgSO_4$, $AlPO_4$, for example.

† Their equation is

$$\Lambda_3 = \Lambda_3^0 - \frac{\Lambda_3^0 \epsilon^2 z_1 z_2}{3DkT}\left(\frac{\beta_1}{1+\beta_0} + \frac{\beta_2}{\alpha+\beta_0}\right)\kappa - \frac{\epsilon z_3 \kappa 96{,}500}{6(300)\pi\eta}$$

where

$$\alpha^2 = \frac{z_1\omega_1 + z_2\omega_2}{(z_1+z_2)(\omega_1+\omega_2)}$$

$$\omega \sim \frac{\Lambda_i^0}{z}$$

$$\beta_0^2 = \left(\frac{z_1\omega_1}{\omega_1+\omega_3} + \frac{z_2\omega_2}{\omega_2+\omega_3}\right)\cdot\frac{1}{z_1+z_2}$$

(positive) ion present in vanishingly small quantities in a solution composed of ions 1 and 2 predicts that the hydrogen ion should move more slowly in 0.1 *N* potassium chloride solution than it does in 0.1 *N* hydrochloric acid and that the potassium ion should move faster in the 0.1 *N* hydrochloric acid than it does in 0.1 *N* potassium chloride solution. Longsworth's data are in qualitative agreement with this interesting prediction.

The Conductance of Concentrated Solutions.—In extending the Debye, Hückel, and Onsager theory to higher concentrations, there are several factors to consider in addition to the solution of mathematical difficulties. Onsager's equation (6) contains, among other quantities, the dielectric constant of the solvent D, the viscosity of the solvent η, and the mobilities of the ions at infinite dilution. There is no reason for believing that the dielectric constant of the solvent in concentrated solutions is equal to that of pure water. Furthermore, it is not immediately evident that a macroscopic measurement of the dielectric constant of the solution would give a value for the dielectric constant suitable for inclusion in the Onsager equation, since the resultant dielectric constant of the solution may not be that in the immediate neighborhood of an ion. Up to the present time different methods of measuring the dielectric constant of conducting solutions have given widely varying results, so that it is impossible to state with certainty what is the magnitude of the dielectric constant.

Much less uncertainty is attached to the measurement of the viscosity of solutions. It is well known that viscosity measurements can be made with excellent accuracy, and although the significance of the results has been greatly clarified in recent times, we are yet uncertain as to the correct relation between the measured viscosity of the solution and the mobility of the ions.

$$\beta_1 = \frac{z_3}{z_1 + z_2}\left[\frac{(z_1\omega_1 - z_3\omega_3)(1 - \alpha^2) + z_2\omega_3\alpha^2}{-z_2(\omega_1 + \omega_3)(1 - \alpha^2)} + \frac{(z_2\omega_2 + z_3\omega_3)(1 - \alpha^2) + z_1\omega_3\alpha^2}{z_1(\omega_2 + \omega_3)(1 - \alpha^2)}\right]$$

and

$$\beta_2 = \frac{z_3}{z_1 + z_2}\left(\frac{\omega_3}{\omega_1 + \omega_3} - \frac{\omega_3}{\omega_2 + \omega_3}\right)\frac{\alpha^2}{1 - \alpha^2}.$$

Jones and Dole* found that the relative fluidity φ, the reciprocal of the relative viscosity, of solutions of strong electrolytes could be expressed up to a high concentration by the equation (see Fig. 2)

$$\varphi = \frac{1}{\eta} = 1 - A\sqrt{c} \pm B(c). \tag{11}$$

Jones and Dole expressed the idea that the Debye theory of interionic attractions could account for the square-root term and

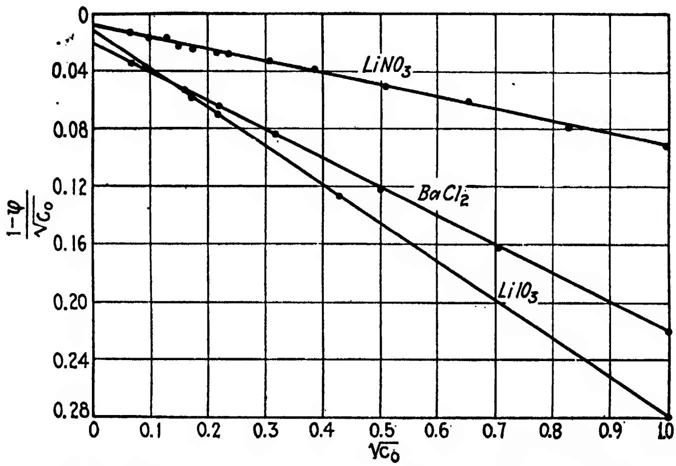

FIG. 2.—Relative fluidity of barium chloride, lithium iodate, and lithium nitrate as a function of the concentration.

the A constant of Eq. (11). Falkenhagen and Dole† tested this idea from a mathematical standpoint and were able to confirm the hypothesis of Jones and Dole. As regards the viscosity correction to the conductance values these theoretical viscosity studies indicate that no correction should be applied, at least in the region of dilute solutions. This is because the change of equivalent conductance and the change of relative viscosity are due in part to exactly the same effect, *viz.*, the distortion of the symmetrical ionic atmosphere as the ions move through the solutions. Although the macroscopic viscosity of the system has

* GRINNELL JONES and M. DOLE, *J. Am. Chem. Soc.*, **51**, 2950 (1929).

† H. FALKENHAGEN and M. DOLE, *Physik. Z.*, **30**, 611 (1929); *Z. hysik. Chem.*, **B 6**, 159 (1929). H. FALKENHAGEN and E. L. VERNON, *physik. Z.*, **33**, 140 (1932); *Phil. Mag.*, (7) **14**, 537 (1932).

been altered by the electrical effects operating between ions at a distance, the viscosity of the solvent between the ions may not have been altered, as Jones and Dole* point out. Experimental evidence supporting the viewpoint of Jones and Dole seems to be afforded by data obtained by MacInnes and Cowperthwaite† on the ionic conductances of the chloride ion in 0.1c solutions of sodium and potassium chloride at 25°C. These data are shown in Table IV along with the corresponding values of the measured relative viscosities (the viscosities are at $\frac{1}{8}c$ and were obtained by Wagner and Reyher). The viscosities are seen to differ by

TABLE IV.—COMPARISON OF IONIC CONDUCTANCES AND SOLUTION VISCOSITIES AT 25°C.

Salt	Λ_{Cl}	η
NaCl	65.54	1.013
KCl	65.53	0.993

2 per cent, while the ionic conductances uncorrected for the viscosity are practically identical. This would seem to indicate that the macroscopic viscosity and mobility are in no way related at this concentration. In very concentrated solutions it may be necessary to apply a viscosity correction, but the proper type of experiment to answer this question has not been performed yet.

However, if the viscosity of the solvent is changed by change of temperature or by change of pressure, the mobility of the ions will change. Increase of temperature decreases the viscosity of water to the extent of 2.5 per cent per degree centigrade at 18°. The conductance of a large number of solutions increases to the extent of approximately 2.5 per cent per degree, thus indicating a very close connection between conductance and viscosity. The conductances of the hydrogen and hydroxyl ions are not increased as much by rise of temperature as are the conductances of most ions. The reason for this will be considered in connection with quantum mechanical theories of electrochemistry.

* GRINNELL JONES and M. DOLE, *J. Am. Chem. Soc.*, **52**, 2245 (1930).

† D. A. MACINNES and I. A. COWPERTHWAITE, *Trans. Faraday Soc.*, **23**, 400 (1927).

TABLE V.—CONDUCTANCE AND VISCOSITY AS A FUNCTION OF TEMPERATURE

$t°$, C.	η_{H_2O}	0.01N KCl		0.01N HNO_3	
		Λ	$\eta\Lambda$	Λ	$\eta\Lambda$
0	0.01794	77.28	1.386	253	4.54
18	0.01060	122.18	1.295	364	3.86
25	0.008949	141.18	1.263	406	3.63
50	0.005492	215.10	1.181	547	3.00
75	0.003806	295.00	1.123	675	2.57
100	0.002839	376.00	1.067	785	2.23

Table V contains values for the equivalent conductance of 0.01 N nitric acid and potassium chloride at different temperatures and the viscosity of water at the same temperatures. If viscosity decrease with rise of temperature were the sole factor influencing the rise in conductance with rise of temperature, one would expect the product $\Lambda\eta$ to be a constant. It is more nearly a constant for potassium chloride solutions than for nitric acid, yet the definite decrease of $\Lambda\eta$ with rise of temperature indicates that factors other than a decrease in viscosity will have to be considered.

The connection between change of viscosity with change of pressure and change of conductance with change of pressure is not so clear as in the case of the temperature coefficients. This is clearly seen in Table VI where the ratios η_0/η and Λ/Λ_0 for 0.01 N potassium chloride should always be equal if the conductance is inversely proportional to the viscosity and if no other disturbing effects enter in.* At the low pressures the conductance actually increases despite the increase in viscosity. Zisman concludes that the size of the ions must decrease with increasing pressure in order to account for the larger values of $\Lambda/\Lambda_{p=0}$.

It is possible that the effective size of the ions may change with change of concentration. Onsager introduced in his final equation the molal conductance at zero concentration; this quantity is inversely proportional to the ion size, the smaller the ion, the greater is its limiting conductance. If the ion size changes with change of concentration, it is the same as saying

* Data from W. A. ZISMAN, *Phys. Rev.*, **39**, 151 (1932).

TABLE VI.—DATA FOR POTASSIUM CHLORIDE 0.01 N AQUEOUS SOLUTION AT 30°C.

Press., kg./cm.[2]	$\eta_{p=0}/\eta$	$\Lambda/\Lambda_{p=0}$
250	0.988	1.0049
1,250	0.937	1.0070
2,250	0.872	0.986
3,500	0.780	0.937
4,500	0.710	0.891
5,500	0.648	0.842
6,500	0.595	0.790
7,500	0.550	0.738
8,500	0.512	0.689
9,500	0.478	0.642

that $\bar{\Lambda}_0$ as introduced into Onsager's equation changes; for $\bar{\Lambda}_0$ indirectly represents the size of the ions. Of course, $\bar{\Lambda}_0$ has a perfectly definite and fixed meaning; it is the limiting conductance to which the molal conductance approaches as the concentration approaches zero. $\bar{\Lambda}_0$, as used in Onsager's equation, should be replaced by a function which will take into account a possible change in the size of the ion.

The great difficulty with the theoretical interpretation of the conductance of any electrolyte is the inability to measure directly the concentration of the ions. Referring to Equation (V-18),

$$\Lambda = \alpha F(u + v), \qquad \text{(V-18)}$$

it is evident that we have two unknowns, α and $(u + v)$, but only one equation. If the mass action law is applicable, we have another equation but also another unknown, K. To solve the problem we must either assume as Arrhenius did that $(u + v)$ is independent of the concentration, or assume as Debye did that α is unity or we can make neither of these assumptions, but calculate both α and $(u + v)$ at various concentrations. For exceedingly weak electrolytes where there are few ions present to interact with each other, the assumption of constant $(u + v)$ is valid; for strong electrolytes where there are many ions interacting with each other, the entire variation of the equivalent conductance with change in concentration seems to be due to a change in $(u + v)$ and Debye's assumption is valid; for inter-

mediate electrolytes neither assumption is valid; we must consider possible variations of both α and $(u + v)$ or, in other words, we need both the theory of Arrhenius and that of Debye to explain the data.

The Fusion of the Arrhenius and Debye Theories.—One of the most fruitful applications of the Debye theory is in the field of weak electrolytes. It should always be remembered that the Debye theory is to be considered as an extension or correction to the Arrhenius theory. The Debye theory is not a theory of "complete dissociation"; it requires for its application merely a knowledge of the concentration of the ions. There are no solutions where surer knowledge of the ionic concentration is had than in solutions of weak electrolytes whose conductances obey the Ostwald dilution law. Hence the Debye theory can be applied with considerable rigor to these solutions.

Acetic acid is generally chosen as a typical example of a weak electrolyte and we shall also choose acetic acid for our discussion. Consider an 0.001028c solution of acetic acid whose molal conductance as found by MacInnes and Shedlovsky* is 48.133. Before the Debye theory it was the custom to calculate the degree of dissociation from the equation,

$$\frac{\Lambda}{\Lambda_0} = \alpha. \qquad \text{(V-23)}$$

Applying the datum for 0.001c acetic acid to this equation, the degree of dissociation (since Λ_0 is 390.59) turns out to be

$$\frac{48.133}{390.59} = 0.1232,$$

or the substance is 12.32 per cent dissociated. As stated in Chap. V, we know that Eq. (V-23) should be corrected for any change in the mobility of the ions. As the concentration increases, the concentration of the ions increases, causing the mobility of the ions to decrease due to the electrical interionic attractions. This decrease in ion mobility is just as real an effect for acetic acid as it is for a strong electrolyte and may be treated in accordance with the principles of the Debye theory.

* D. A. MacInnes and T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1429 (1932).

The correct equation for calculating the degree of dissociation is

$$\frac{\Lambda}{\Lambda_0} = \alpha\left(\frac{u + v}{u_0 + v_0}\right), \tag{12}$$

which on rearrangement gives

$$\frac{(u_0 + v_0)}{(u + v)} \frac{\Lambda}{\Lambda_0} = \alpha$$

or

$$\frac{\Lambda}{F(u + v)} = \alpha, \tag{13}$$

since $F(u_0 + v_0) = \Lambda_0$. To calculate the degree of dissociation from Eq. (13) it is necessary to know the mobilities of the ions at the same concentration that the equivalent conductance Λ is measured. Let us call $F(u + v)$ equal to Λ_e in agreement with MacInnes and Shedlovsky; then for acetic acid

$$\Lambda_e = \Lambda_{\mathrm{HCl}} - \Lambda_{\mathrm{NaCl}} + \Lambda_{\mathrm{NaOAc}}, \tag{14}$$

where Λ_{HCl} is the conductance of the hydrochloric acid at the same *ionic* concentration that Λ_{HOAc} is measured. Λ_{NaCl} nd Λ_{NaOAc} are also conductances measured at the same ionic concentration that Λ_{HOAc} is measured. Λ_e gives the sum of the mobilities of the hydrogen and acetate ions at the concentration in question and may be considered as the limiting conductance value corrected for the mobility change due to the interionic electrical effects. Λ_e may also be considered the equivalent conductance of the acetic acid calculated in the usual manner except that the concentration of the ions is used in the equation $\Lambda = 1{,}000\kappa/N$ instead of the stoichiometrical concentration. This "ionic" equivalent conductance would obey the square-root law since it represents the conductance of acetic acid that is completely dissociated. The calculation based on Eq. (14) assumes that hydrochloric acid, sodium chloride, and sodium acetate are completely dissociated. We know this to be true without sensible error because at this very low concentration the Onsager equation is valid when we take the concentration of the ions as equal to the stoichiometric concentration. In order to find Λ_e for acetic acid at $0.001c$ it is first necessary to make an approximate calculation of the concentration of the ions in acetic acid in order

to find the concentration at which to take the conductance values for hydrochloric acid, sodium chloride and acetate in Eq. (14). This is done by means of the degree of dissociation, α, as calculated by Eq. (V-23). The concentration of the ions will be

$$c\alpha = c_i = (0.001)(0.1232) = 1 \times 10^{-4} \text{ approximately.} \qquad (15)$$

The limiting conductance for acetic acid, Λ_e, at this concentration is, from Eq. (14),

$$\Lambda_e = 424.48 - 125.54 + 90.17 = 389.11, \qquad (16)$$

and the degree of dissociation is

$$\alpha = \frac{\Lambda}{\Lambda_e} = \frac{48.133}{389.11} = 0.1237 \qquad (17)$$

instead of the former value of 0.1232. With this new figure for the fraction dissociated, a new ionic concentration can be calculated and a new value for Λ_e obtained. Actually MacInnes and Shedlovsky calculate after three approximations that at an acetic acid concentration of 0.001028c, Λ_e is 388.94, and the degree of ionization is

$$\frac{48.133}{388.94} = 0.1238. \qquad (18)$$

It is possible to apply the above method of calculating α to many other acids both stronger and weaker than acetic acid. The stronger the acid, the greater will be the difference between Λ_0 and Λ_e. With strong electrolytes, such as hydrochloric acid, the decrease in mobility is the entire effect (so far as it is possible to judge) and Λ_e becomes equal to Λ. Looking at the subject from this point of view we see that there is no essential difference between a strong and weak electrolyte; it is merely one of degree. We also see that the Debye theory does not displace the Arrhenius theory, but merely modifies and improves it.

Exercises

1. Calculate the force in dynes which exists between two like unit charges 1×10^{-8}, 1×10^{-7} and 1×10^{-6} cm. apart in a medium of dielectric constant 80 and unity.

2. Calculate the value of the Onsager equation constant for sodium chloride taking Λ^0_{NaCl} equal to 126.42 at 25°C. in water. The dielectric constant is equal to 78.6 and the viscosity is 0.00891.

3. Test the Onsager equation by means of the following equivalent conductance data for sodium chloride (data of Shedlovsky) at 25°C.:

N	Λ_{NaCl}
0.0001	125.56
0.0002	125.21
0.0005	124.50
0.001	123.72
0.002	122.67
0.005	120.58
0.01	118.43

CHAPTER VII

THEORETICAL INTERPRETATION OF THE CONDUCTANCE OF ELECTROLYTES

III. THE WIEN EFFECT AND THE DEBYE FREQUENCY EFFECT

The combined Debye-Arrhenius theory of conductance proves to be particularly fruitful in explaining and interpreting a new phenomenon recently discovered known as the Wien effect. The Jena physicist, Wien, and his coworkers were investigating the temperature coefficient of the equivalent conductance under high potentials and under conditions in which the current was allowed to flow through the conductance cell for a very short time, when they discovered a curious effect which they, at first, were more or less unable to explain. They discovered that the equivalent conductance of the solutions increased as the applied potential increased more than one should expect just from the heating effect of the current alone. Ohm's law is $I = (1/R)E$, and as E increases, I should increase in the same proportion so that $1/R$ should remain constant. But in Wien's experiments, I increased more than it should according to Ohm's law; hence, under the conditions of a very high applied field strength we must conclude that Ohm's law is invalid for electrolytic solutions.

Now it must be remembered that an electric current passing through the conductance cell generates heat in accordance with the equations given in Chap. III. The heating effect is proportional to IE in watts or to $E^2(1/R)$. At very high voltages $E^2(1/R)$ will be large, and we should expect the solutions to be heated considerably so that we might find an explanation of the Wien effect in the increase of conductance with increase of temperature of the solution. This increase of conductance would be due chiefly, as has been explained in Chap. VI, to the decrease in viscosity of the solvent as the temperature is raised. But this

explanation is inadequate to explain the Wien effect* as can be demonstrated in the following manner: In the first place, a quantitative calculation shows that the heating effect is quite inadequate in most cases to account for the increase of conductance. In the second place, it is possible to compare solutions of two different salts by placing two cells containing the two solutions in two different arms of the measuring bridge. If the solutions have the same resistance, the heating effect should be the same in both and the conductance changes nearly the same. But this is actually not the case; in a particular cell Wien showed that at 14,000 v. a barium ferrocyanide solution showed an increase in conductance approximately 35 per cent greater than a solution of sodium chloride. Furthermore, the increase of conductance depends upon the valences of the dissolved ions, their mobilities, and the concentration, all of which could not possibly be explained on the simple heating hypothesis. Neither can the Wien effect be explained on the assumption of a breaking up of complex ions due to the high voltages, since the effect becomes greater as the concentration is lowered. In dilute solutions there should be fewer complex ions, and the voltage effect should be smaller instead of larger as it actually is.

Fortunately, the Debye and Onsager theory of conductance was developed about this time, which in the hands of Joos and Blumentritt† led to an understanding of the Wien effect. When a high potential is applied to a conductance cell, the ions in the solution will, of course, move faster than under conditions of low potential gradient. The usual velocity of an ion during conductance measurements is of the order of magnitude of 0.001 cm. per second, but in Wien's experiments the ions traveled at the terrific rate of about a meter per second. Because of these abnormal velocities we should hardly expect that the ionic atmosphere about the ion could form in the same way that it does when the ion is moving slowly. Indeed a calculation

* References for the Wien effect are as follows: J. Malsch and M. Wien, *Physik. Z.*, **25**, 559 (1924); *Ann. Physik*, **83**, 307 (1927); M. Wien, *Ann. Physik*, **83**, 327 (1927); *Physik. Z.*, **28**, 834 (1927); *Ann. Physik*, **85**, 795 (1928); *ibid.*, (5) **1**, 400 (1929); J. Schiele, *Ann. Physik*, **13**, 811 (1932); P. Debye, *Z. Elektrochem.*, **39**, 478 (1933).

† Joos and Blumentritt, *Physik. Z.*, **28**, 836 (1927); Blumentritt, *Ann. Physik*, **85**, 812 (1928); (5) **1**, 195 (1929).

shows that the ion in these high electric fields is moving so rapidly that it migrates several thicknesses of the ionic atmosphere during a time equal to its relaxation time; hence we must conclude that the ionic atmosphere about an ion does not have time to form. The relaxation time θ is given by the equation

$$\theta = \frac{z_1 + z_2}{(\Lambda_1 + \Lambda_2)} \frac{15.3 \times 10^{-8}}{kT\kappa^2}. \tag{1}$$

Under these conditions of zero ionic atmosphere the electric forces of relaxation and the electrophoretic force do not exist (the electrophoretic force does not exist because the ion is no longer moving in a stream of oppositely charged ions); hence the ion should migrate with the velocity that it would have at zero concentration, where the electric force of relaxation and the electrophoretic force are also zero. Keeping this physical picture in mind, we should expect the limiting value to be attained at a lower potential gradient when the concentration of the electrolyte is lower because the time of relaxation increases with the dilution. The longer the time of relaxation, the more difficult will it be for the ionic atmosphere to form and the easier will it be for the conductance to attain the theoretical value. Wien has expressed these ideas in the manner illustrated in Fig. 1.

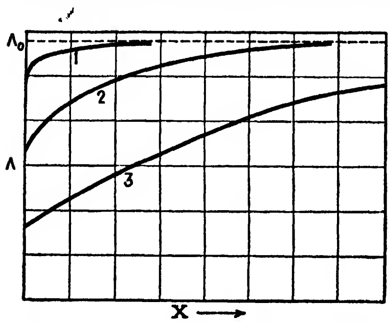

FIG. 1.—The Wien effect, showing the tendency of the equivalent conductance to approach the limiting conductance (dotted line) at infinite dilution as the field strength X is increased. Curves 1, 2, and 3 represent very dilute solutions, dilute solutions, and somewhat more concentrated solutions respectively.

Onsager, in his theoretical conductance calculations, made the simplifying assumption that the distortion of the ionic atmosphere was directly proportional to applied field strength, but at very high field strengths this is not true. As Blumentritt points out, to obtain a correct theory for the conductance under high fields it is necessary to consider the higher terms (which include X, the field strength in the x-direction) in the nonlinear differential equation. The result obtained by Blumentritt for the

potential, possessing only an x-component, at the position of the considered ion due to the surrounding ionic atmosphere (the relaxation effect) is

$$\psi = (a_1X - a_3X^3 + a_5X^5 - + \cdots)x, \tag{2}$$

whereas Onsager obtained an expression for ψ in terms of X and without any higher powers of X. Blumentritt also found that the electrophoretic force was capable of being developed in uneven powers of X. Combining the two forces and calculating the change of Λ with change of field strength, Blumentritt obtains

$$\frac{\Lambda_X - \Lambda_{X=0}}{\Lambda_{X=0}} = \Delta\Lambda = AX^2(1 - BX^2) + \cdots \tag{3}$$

where

$$A = \frac{\epsilon^2\sqrt{1000}}{(kT)^{2.5}\sqrt{4\pi\mathbf{N}}(300)^2} \cdot \frac{z_1z_2(z_1 + z_2)^{1.5}q^{2.5}\kappa_1}{\sqrt{DN}(1 - q)^3 f_\Lambda} + \frac{4.83 \times 10^{-7}\epsilon}{6(\pi kT)^{3/2}\sqrt{\mathbf{N}}(300)^2} \cdot \frac{\sqrt{D}z_1 \cdot z_2\sqrt{z_1 + z_2}q^{1.5}}{\sqrt{N}(1 + \sqrt{q})^2\Lambda\eta} \tag{4}$$

$$B = \frac{1000}{4\pi\mathbf{N}kT(300)^2}\frac{\kappa_2}{\kappa_1} \cdot \frac{D(z_1 + z_2)q}{N(1 - q)^2} \tag{5}$$

$$q = \frac{(u_1 + u_2)z_1z_2}{(z_1 + z_2)(z_2u_1 + z_1u_2)} \tag{6}$$

$$\kappa_1 = 0.075 - 0.2\sqrt{q} + 0.15q - 0.025q^2 \tag{7}$$

$$\kappa_2 = 0.00558 - 0.06696q + 0.14286q^{1.5} - 0.10045q^2 + 0.02232q^3 - 0.00335q^4 \tag{8}$$

and

$$f_\Lambda = \frac{\Lambda}{\Lambda_0}. \tag{9}$$

The theoretical calculation of Blumentritt is valid only for not too high field strengths. In order to test Blumentritt's equations Wien* carried out some measurements on the conductance change due to potential gradients up to 30,000 v. per centimeter. He found that his results could be expressed by the equation

$$\Delta\Lambda = aE^2 - bE^4, \tag{10}$$

where a and b are constants and E is the applied voltage. The accuracy with which Eq. (10) can reproduce the data is shown in Table I.

* M. Wien, *Ann. Physik*, **85**, 795 (1928).

TABLE I.—WIEN EFFECT FOR $Ba_3[Fe(CN)_6]_2$ AT κ = 0.000125 OHM^{-1} CM.$^{-1}$

$E/10{,}000$	$\Delta\Lambda_{obs.}$	$\Delta\Lambda_{calcd.}$
4.47	0.06	0.06
7.96	0.21	0.18
11.3	0.35	0.35
14.3	0.55	0.55
17.4	0.77	0.77
20.3	1.00	1.00
26.1	1.49	1.43
31.7	2.02	1.74
37.3	2.51	1.78

Examining Table I we see that up to 20,000 v. per centimeter an equation of the form of Eq. (10) is very accurately valid. Blumentritt has compared her theoretical A and B constants, Eq. (3), with the experimental A and B constants obtained by Wien. The agreement, which in some cases is good and in others bad, is illustrated in Tables II and III.

TABLE II.—TEST OF BLUMENTRITT'S THEORETICAL EQUATION (3) AT 18°C. A VALUES

Salt	N	$A.10^{11}$		N	$A.10^{11}$		N	$A.10^{11}$	
		Calcd.	Obs.		Calcd.	Obs.		Calcd.	Obs.
$MgSO_4$	0.00605	1.12	1.49	0.00272	1.50	1.96	0.00127	2.0	2.5
$MgCrO_4$	0.00574	1.14	1.21	0.00265	1.55	1.60	0.00126	2.1	1.8
$K_3Fe(CN)_6$	0.00350	0.73	0.44	0.00168	1.0	0.70	0.00082	1.4	0.77
$K_4Fe(CN)_6$	0.00363	1.07	0.88	0.00172	1.5	1.17	0.00083	2.0	0.82
$Ba_3[Fe(CN)_6]_2$	0.00515	3.2	3.9	0.00225	4.2	5.1	0.00094	5.4	5.6
$Ba_2Fe(CN)_6$	0.00575	4.2	6.6	0.00260	5.5	10.9	0.00108	7.2	11.6

For the case of very high electric fields, from 20,000 to 40,000 v. per centimeter, the conductance approaches a limiting value as has been stated before, the limiting value being of the order of magnitude of the equivalent conductance at infinite dilution. The experimental proof of this statement depends upon a knowledge of the correct conductance value at infinite dilution, and in the case of the solutions that Wien worked with, these values are more or less uncertain; hence we may conclude at the present time

that it is only qualitatively correct to say that the maximum conductance obtained as the field strength is raised is equal to the equivalent conductance at zero concentration (the latter value taken at low field strength).

TABLE III.—TEST OF BLUMENTRITT'S THEORETICAL EQUATION (3) AT 18°C. *B* VALUES

Salt	*N*	*B*. 10^{11}		*N*	*B*. 10^{11}		*N*	*B*. 10^{11}	
		Calcd.	Obs.		Calcd.	Obs.		Calcd.	Obs.
$MgSO_4$	0.00605	1.2	1.7	0.00272	2.8	2.3	0.00127	6.0	6.0
$MgCrO_4$	0.00574	1.3	3.0	0.00265	2.8	3.6	0.00126	6.0	7.5
$K_3Fe(CN)_6$	0.00350	2.0	1.1	0.00168	4.2	1.5	0.00082	8.7	3.4
$K_4Fe(CN)_6$	0.00363	2.1	2.3	0.00172	4.5	2.9	0.00083	9.4	(3.8)
$Ba_3[Fe(CN)_6]_2$	0.00515	1.7	2.1	0.00225	3.8	4.5	0.00094	9.2	7.5
$Ba_2Fe(CN)_6$	0.00575	2.2	3.2	0.00260	5.0	3.9	0.00108	12.0	(6.9)

Falkenhagen* has recently given a qualitative mathematical explanation of the Wien effect at high field strengths.

A most interesting phase of the Wien effect is Wien's work on the conductance changes of weak electrolytes. Wien investigated various organic acids such as acetic acid, and although he had expected a very small increase in the conductance due to the presence of very few ions in the acetic acid solutions, he found, much to his surprise, a very large increase in the conductance on increasing the field strength. The increase was much larger than that shown by corresponding strong acids like sulfuric acid. Figure 2 illustrates the conductance increase with increasing applied voltage for various weak organic acids and sulfuric acid. An examination of Fig. 2 shows that the Wien effect is more pronounced the weaker the acid. Sulfuric acid is the strongest

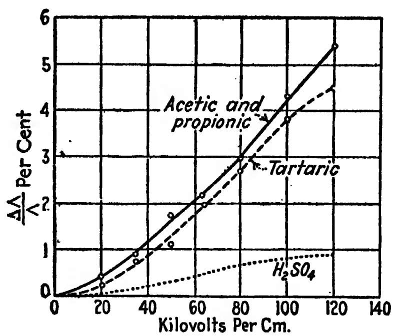

FIG. 2.—The Wien effect for some weak organic acids and sulfuric acid using hydrochloric acid in the comparison cell.

* H. FALKENHAGEN, *Physik. Z.*, **32**, 353 (1931).

acid, and both the first and second dissociation constants of tartaric acid are greater than the dissociation constants of acetic and propionic acids (the dissociation constant is a measure of the strength of an acid and will be considered later). The relation between the Wien effect and the degree of dissociation of the acid is also clearly shown in the comparison of the conductance increases in solutions of acetic and monochloroacetic

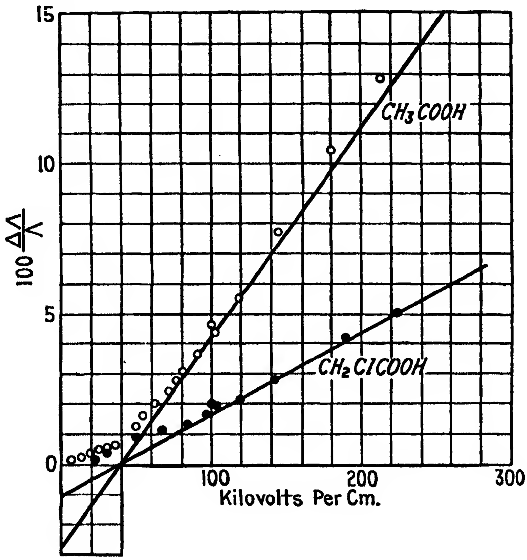

FIG. 3.—Wien effect for acetic and chloroacetic acids using hydrochloric acid in the comparison cell. Solid lines represent Onsager's theoretical calculations.

acids, Fig. 3. Monochloroacetic acid is a much stronger acid than acetic acid, and as can readily be seen, gives a smaller Wien effect than does acetic acid. It is evident, then, that Wien has discovered an important relation between the conductance increases on increasing the applied voltage and the strength of the acid or the degree of dissociation.*

Onsager† has apparently given the correct explanation of this remarkable behavior in terms of an enhanced dissociation of the

* M. WIEN, *Physik. Z.*, **32**, 545 (1931); J. SCHIELE, *Ann. Physik*, (5) **13**, 811 (1932).

† L. ONSAGER, *J. Chem. Phys.*, **2**, 599 (1934).

weak electrolyte. True equilibrium between the ions and the undissociated molecules cannot exist in the presence of an external electric field; in order to discover the effect of the field on the dissociation it is necessary to develop a kinetic theory for the electrolytic dissociation and recombination of ions based on the laws of Brownian motion. A detailed mathematical analysis indicates that the rate of recombination of the ions is independent of the field, but that the rate of dissociation depends on the field, the computed relative increase of the dissociation constant being given by the formula

$$\frac{K_X}{K_{X=0}} = 1 + 2\beta Q + \frac{(4\beta Q)^2}{2!\,3!} + \frac{(4\beta Q)^3}{2!\,3!} + \cdots,$$

where

$$Q = \frac{q_1 q_2}{2DkT} > 0,$$

and

$$2\beta = \frac{|X(q_1\omega_1 + q_2\omega_2)|}{kT(\omega_1 + \omega_2)}.$$

Here, $kT\omega_i$ are the coefficients of diffusion and $q_i\omega_i$ the velocities of electrolytic migration in a field of 1 e.s.u. (= 300 v. per centimeter). Onsager has tested his theoretical equation by means of the data for acetic acid and chloroacetic acid illustrated in Fig. 3. The solid lines represent the theoretical calculations, while the circles are the experimental results. The agreement is striking, particularly when one considers that the computation of the theoretical curves involves the adjusting of no empirical constants. It is interesting to note that the change in the dissociation constant due to the increased field as predicted by Onsager's equation is independent of the concentration. In the region of weak fields, however, this last statement is not true; a complete theory based on no approximations would yield values of $K_X/K_{X=0}$ dependent on the concentration.

It is interesting to consider briefly Wien's experimental method* for measuring the conductance of electrolytes under high field strengths. His apparatus is diagrammed schematically in Fig. 4.

In Fig. 4, R_1 and R_2 are the resistances of the electrolytic cells, F a variable resistance (spark gap), C a large condenser, L an

* J. Malsch and M. Wien, *Ann. Physik*, **83**, 305 (1927).

inductance, and L_1 and L_2 inductances for coupling the current that flows through the main circuit with the detecting circuit M_1, M_2, etc. A source of potential, not shown in the diagram, builds up the potential across the plates of the condenser C until the potential is sufficient to cause a "break down" of the dielectric at F. When this occurs, the air between the spark gap ionizes so that the resistance of the spark gap drops to a very small quantity; the total resistance of the circuits FAL_1 and FAL_2 now approaches that of the resistances R_1 and R_2 and the greatest part of the potential drop occurs across R_1 and R_2. The potential of the condenser can be built up to very high values by increasing the distance between the sparking points at F. The duration

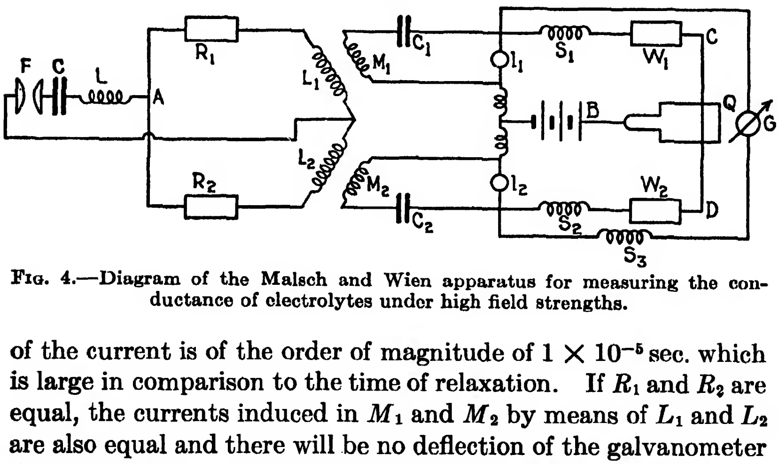

FIG. 4.—Diagram of the Malsch and Wien apparatus for measuring the conductance of electrolytes under high field strengths.

of the current is of the order of magnitude of 1×10^{-5} sec. which is large in comparison to the time of relaxation. If R_1 and R_2 are equal, the currents induced in M_1 and M_2 by means of L_1 and L_2 are also equal and there will be no deflection of the galvanometer G. The detecting circuit is essentially a Wheatstone bridge; W_1 and W_2 are two variable resistances which are equalized by fine adjustment of the mercury contact Q along the manganin slide wire, CD. S_1 and S_2 are two inductances whose purpose is to offer a high frequency resistance to the current induced in M_1 and M_2 so that the induced current will be required to flow through the two Osram (similar to Mazda) lamps, l_1 and l_2. If the induced currents that momentarily flow through the two lamps are unequal, the lamps will be heated a different amount and their direct-current resistance will vary, causing the equilibrium in the Wheatstone bridge to be upset and the galvanometer to show a deflection. But by adjustment of R_1 and R_2 to equality, the lamps will be heated to an equal extent, causing

no galvanometer deflection. The inductance S_3 is inserted into the galvanometer circuit to balance out any extraneous currents that are induced in the bridge by the main source of current. This method is very accurate; the error is of the order of magnitude of a few parts in ten thousand.

The Debye Frequency Effect.—Undoubtedly inspired by the work of Wien on high electric-field strengths, Debye and Falkenhagen* were led to consider theoretically the effect on electrolytic conductances of an alternating current of very high frequency; this effect is called the dispersion of the conductance. From a physical standpoint the Debye frequency effect may be considered as being quite the opposite of the Wien voltage effect. In the Wien effect the ions were moving so fast that the ionic atmosphere became extraordinarily distorted, so distorted in fact that the ionic atmosphere about the ion could not form. In the Debye effect the ionic atmosphere is symmetrical and is not distorted at all. This is because the electric current changes its direction so frequently (and in a shorter time than its time of relaxation) that the ion may be considered as practically standing still. Under these stationary conditions, the symmetrical ionic atmosphere fails to be distorted, and as a consequence the ionic atmosphere exerts no retarding force upon the motion of the ion. Hence, as the frequency of the electric current increases, the conductance of the current should also increase. This is true as regards the electric force of relaxation which depends for its origin upon an unsymmetrical ionic atmosphere. But the electrophoretic force will exist, due to the fact that the ionic atmosphere is built up; hence the braking force of electrophoresis will be independent of the frequency. Thus, from a theoretical standpoint, as the frequency increases, the conductance should increase, but not to the extent it increases in the Wien effect, because the electrophoretic force must still be considered.

Let us write the molal conductance $\bar{\Lambda}$ as the sum of the conductance at infinite dilution, $\bar{\Lambda}_0$, the conductance change due

* P. Debye and H. Falkenhagen, *Physik. Z.*, **29**, 401 (1928); *Z. Elektrochem.*, **34**, 562 (1928); H. Gaertner, *Physik. Z.*, **32**, 919 (1931); M. E. Spaght, *Physik. Z.*, **33**, 534 (1932); see the following reviews: H. Falkenhagen and J. W. Williams, *Z. physik. Chem.*, A **137**, 399 (1928); *J. Phys. Chem.*, **33**, 1121 (1929); *Chem. Rev.*, **6**, 317 (1929); P. Debye, *Z. Elektrochem.*, **39**, 478 (1933).

to the electric force of relaxation, $-\bar{\Lambda}_{\mathrm{I}}$, and the conductance change due to the electrophoretic force $-\bar{\Lambda}_{\mathrm{II}}$; then

$$\bar{\Lambda} = \bar{\Lambda}_0 - \bar{\Lambda}_{\mathrm{I}} - \bar{\Lambda}_{\mathrm{II}}. \tag{11}$$

From Debye and Falkenhagen's calculations

$$\bar{\Lambda}_{\mathrm{I}} = \frac{\epsilon z_1 z_2}{3DkT}\kappa\bar{\Lambda}_0 f(x) \tag{12}$$

where

$$f(x) = \frac{\sqrt{q}}{\left(1 - \frac{1}{q}\right)^2 + \omega^2\theta^2}\left[\left(1 - \frac{1}{q}\right)\left(\bar{R} - \frac{1}{\sqrt{q}}\right) + \omega\theta\bar{Q}\right] \tag{13}$$

and

$$\bar{R} = \frac{1}{\sqrt{2}}\sqrt{\sqrt{1 + \omega^2\theta^2} + 1}. \tag{14}$$

$$\bar{Q} = \frac{1}{\sqrt{2}}\sqrt{\sqrt{1 + \omega^2\theta^2} - 1}. \tag{15}$$

The quantities q and θ are given by

$$q = \frac{(\Lambda_{0,1} + \Lambda_{0,2})(z_1 z_2)}{(z_1 + z_2)(\Lambda_{0,1}z_2 + \Lambda_{0,2}z_1)} \tag{16}$$

and

$$\theta = \text{time of relaxation} = \frac{(z_1 + z_2)}{(\Lambda_{0,1} + \Lambda_{0,2})}\,\frac{15.34 \times 10^{-8}}{kT\kappa^2}. \tag{17}$$

The electrophoretic effect Λ_{II} is independent of the frequency $\omega/2\pi$ as the following equation shows:

$$\bar{\Lambda}_{\mathrm{II}} = \frac{\epsilon^2(n_1 z_1^2 + n_2 z_2^2)}{6\pi\eta}\,\frac{1{,}000}{c}\,\frac{\kappa}{9 \times 10^{11}}. \tag{18}$$

From these equations it may be seen that the dispersion of the conductance is a complicated function of the frequency, the valence and mobility of the ions, and it is also a complicated function of the concentration, since θ is inversely proportional to the concentration.

Wien* has been able to test Eq. (12) experimentally. He obtains results in fair agreement with the theory.

* M. Wien, *Ann. Physik*, (5) **11**, 429 (1931). See this paper also for a study of the change of dielectric constant with change of concentration according to the square-root law and with change of frequency.

CHAPTER VIII

THEORETICAL INTERPRETATION OF THE CONDUCTANCE OF ELECTROLYTES

IV. NONAQUEOUS SOLUTIONS

The study of equivalent conductances in nonaqueous solutions is of importance not only in order to discover the nature of these solutions, but also to test the various theories of conductance that have been developed in the study of the conductances in aqueous solutions.

Frazer and Hartley, and Unmack, Murray-Rust, and Hartley* have measured the equivalent conductance of a number of uniunivalent and biunivalent salts in methyl alcohol solutions. The thiocyanates of Li, Na, K, Rb, Cs, and NH_4 give results that are in excellent agreement with the Onsager conductance theory. This is not true, however, for solutions of Mg, Ca, Sr, and Ba thiocyanates. The nitrates of potassium, rubidium, and cesium give solutions whose observed conductances decrease more rapidly as the concentration increases than they should theoretically. It is interesting to note, however, that all of the data, except the results for cadmium and zinc thiocyanates give straight lines in the most dilute region when plotted as a function of the square root of the concentration. Unmack, Murray-Rust and Hartley have calculated the Onsager theoretical slope, $A_{calcd.}$, of the conductance curve and have compared the theoretical slopes with the experimentally observed values, $A_{obs.}$. These data are collected together in Table I, where Δ represents the percentage deviation, $\frac{A_{obs.} - A_{calcd.}}{A_{calcd.}} \times 100$.

* Frazer and Hartley, *Proc. Roy. Soc.* (London), A **109**, 351 (1925); Unmack, Murray-Rust, and Hartley, *Proc. Roy. Soc.* (London), A **127**, 228 (1930). For ethyl alcohol solutions see M. Barak and Harold Hartley, *Z. physik. Chem.*, A **165**, 272 (1933).

TABLE I.—TEST OF THE ONSAGER EQUATION IN DILUTE METHYL ALCOHOL SOLUTIONS AT 25°C.

Salt	Λ_0	$A_{obs.}$	$A_{calcd.}$	Δ	Salt	Λ_0	$A_{obs.}$	$A_{calcd.}$	Δ
LiCNS	101.8	253	255	− 1	$Sr(CNS)_2$	122.0	980	550	
NaCNS	107.0	255	260	− 2	$Ba(CNS)_2$	122.5	850	552	
KCNS	114.5	268	268	0	KCl	105.0	261	258	+ 1
RbCNS	118.2	271	271	0	RbCl	108.6	281	262	+ 7
CsCNS	123.2	304	276	+10	CsCl	113.6	293	267	+10
NH_4CNS	118.7	279	271	+ 3	$LiNO_3$	100.2	250	254	− 2
LiCl	90.9	224	245	− 9	$NaNO_3$	106.4	288	260	+ 1
NaCl	96.9	230	250	− 8	KNO_3	114.5	345	268	+29
$Mg(CNS)_2$	120.0	2,000	545		$RbNO_3$	118.1	355	273	+30
$Ca(CNS)_2$	122.0	1,400	550		$CsNO_3$	122.9	379	276	+37

Williams* concludes "that the chief difficulty rests not with the experimental determination of the mobilities which are required for the (theoretical) calculation . . . , but with the fact that most electrolytes are associated in methyl alcohol solution, even at great dilution." An indication that the conclusion of Williams is probably correct may be obtained from the interesting results of Bauer,† who studied acetone solutions of potassium iodide and lithium bromide.

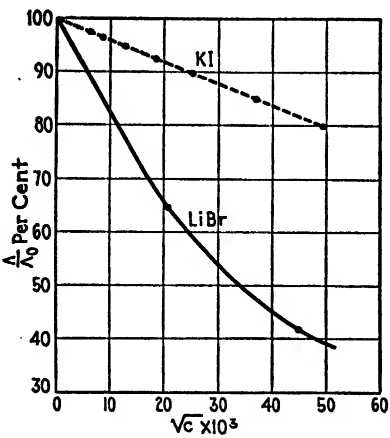

FIG. 1.—The equivalent conductance of potassium iodide and lithium bromide dissolved in acetone as a function of the square root of the concentration.

According to Bauer, acetone solutions of potassium iodide are strong electrolytes while acetone solutions of lithium bromide are not. A plot of the equivalent conductance of potassium iodide against the square root of the concentration gives a straight line, but a similar plot for lithium bromide exhibits the rapid decline in conductance characteristic of weak electrolytes (Fig. 1). Are we to reason from this that the Debye theory is valid for potas-

* J. W. WILLIAMS, *Chem. Rev.*, **8**, 303 (1931).
† F. BAUER, *Ann. Physik*, (5) **6**, 253 (1930).

sium iodide solutions but breaks down entirely for lithium bromide solutions? Or, shall we agree with Williams that the trouble is not with the theory, but with our assumption that the stoichiometric concentration c is the correct concentration of the ions? The answer to these questions may be found in a study of the Wien effect for these two solutions. Bauer's results are illustrated in Fig. 2, and it is readily seen that potassium iodide solutions show the normal Wien effect while lithium bromide solutions show the abnormal Wien effect. This means that lithium bromide dissolved in acetone is only partially dissociated, and is, therefore, in this solvent a weak electrolyte. Hence, we find that we were unjustified in applying the Debye theory to lithium bromide solutions as long as we wrote the stoichiometric concentration equal to the ionic concentration. Bauer's experiments prove that the rapid decrease in conductance of the lithium bromide solutions as the concentration is increased is due to the salt becoming less dissociated. The author believes that many of the apparent contradictions in the Debye theory will be largely eliminated as experiments similar to Bauer's are performed on these "anomalous" solutions.

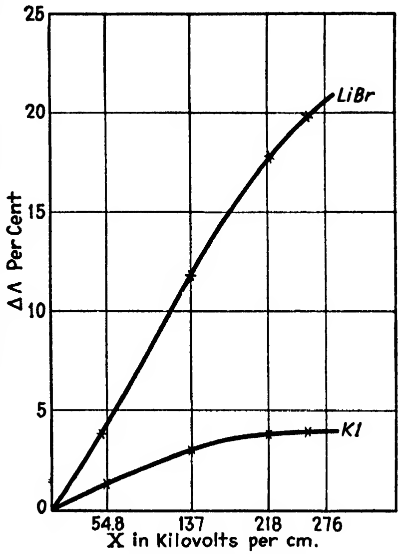

FIG. 2.—The Wien effect for potassium iodide and lithium bromide dissolved in acetone.

Although most of the nonaqueous solutions give results that do not agree so well with the Debye theory as do aqueous solutions, nevertheless it is possible to prepare a solvent with such changed conditions that the Debye theory becomes valid, apparently, up to the very high concentration of half normal. This solvent has the composition, 66 per cent cane sugar in water, and has such a high viscosity that the conductances at infinite dilution are only about 2 per cent of their values in water.

Possner and Wien* have briefly investigated the behavior of some salts in this solvent and have discovered that uniunivalent salts give conductances which agree with the square-root law up to 0.5 N. Salts of higher valence type do not agree so well with the theoretical predictions. The author is at a complete loss to explain this "improvement" in the behavior of the electrolytes due to the addition of sugar, since the dielectric constant of the sugar and water mixture is nearly half that of pure water. The Debye theory is supposed to break down as the dielectric constant is lowered due to the fact that the mathematical approximations in the theoretical calculations become less justified at lower dielectric constants. It may be that the increased viscosity increases the time of relaxation to such an extent that the equations become valid.

It will be remembered that Onsager's equation gives for the change of conductance of a symmetrical salt at constant temperature,

$$\frac{\bar{\Lambda}_0 - \bar{\Lambda}}{\bar{\Lambda}_0} = \left(\frac{k_1}{D^{3/2}} + \frac{k_2}{D^{1/2}\bar{\Lambda}_0\eta}\right)\sqrt{c}, \tag{1}$$

where k_1 and k_2 are constants. Now Walden† has found for the same electrolyte dissolved in a number of solvents that $\bar{\Lambda}_0\eta$ is roughly a constant; hence we can write Eq. (1) as

$$\Delta\bar{\Lambda} = \frac{\bar{\Lambda}_0 - \bar{\Lambda}}{\bar{\Lambda}_0} = \frac{1}{\sqrt{D}}\left[\frac{k_1}{D} + k_3\right]\sqrt{c}. \tag{2}$$

Thus we see that Onsager's equation predicts that a change in the value of $\Delta\bar{\Lambda}$ as one passes to a different solvent depends entirely on the change in the dielectric constant. This prediction is verified in the case of methyl alcohol solutions; the constant multiplying the square root of the concentration is considerably larger due to the lower dielectric constant than the corresponding constant for water. It must be remembered that a decrease in the dielectric constant increases the energy of association according to the theory of Bjerrum and of Fuoss and Kraus (Chap. V) and decreases, therefore, the dissociation.

* H. Possner and M. Wien, *Physik. Z.*, **30**, 161 (1929).

† Walden, *Z. physik. Chem.*, **55**, 207 (1906); *Z. anorg. Chem.*, **113**, 85 (1920).

Conductances in Liquid Ammonia as a Solvent.—A study of the electrical conductances of liquid ammonia solutions is interesting and important chiefly because of the fact that it is possible to dissolve the alkali metals in liquid ammonia and to obtain, thereby, dilute solutions that are similar to electrolytes and concentrated solutions that are similar to metals. Sodium and potassium dissolve in liquid ammonia to give highly colored solutions whose molal conductances exhibit the interesting property of passing through a minimum. At infinite dilution of the metal solution the conductance attains a maximum value of the order of magnitude of 1,034. This value is considerably higher than the molal conductances of salts dissolved in water, and is partly explained on the basis of the low viscosity of the liquid ammonia solutions. As the concentration of the metal in the ammonia is increased, the molal conductance decreases just as does the molal conductance of salts dissolved in water. In this region of concentration, the conductance is electrolytic; that is, the conductance is due to both positive and negative ions, and as a direct current flows through the solution, concentration changes are observed to take place in the neighborhood of the electrodes (see Chap. IX for an explanation of these concentration changes). Kraus,* postulates that sodium, for example, ionizes in liquid ammonia to give the positive sodium ion and the electron as the negative ion. The electron probably combines with, or becomes solvated (ammoniated) with the ammonia molecules so that it does not migrate through the solution with the speed of a free electron. As the concentration increases, the sodium atoms become less ionized so that the molal conductance decreases. A calculation of the ionization values shows that sodium in ammonia is about a hundred times stronger as an electrolyte than is acetic acid in water. In this region of solution concentration, sodium behaves analogously to a salt dissolved in water; but as more metallic sodium is dissolved in the ammonia, the conductance begins to rise instead of continuing to decrease. At a concentration of approximately 0.05 N the molal conductance passes through a minimum value of 478, and above this con-

* C. A. Kraus, "The Properties of Electrically Conducting Systems," Chap. XIV, Chemical Catalog Company, Inc., New York, 1922; W. C. Johnson and A. W. Meyer, *Chem. Rev.*, **8**, 273 (1931).

TABLE II.—EQUIVALENT CONDUCTANCES OF SODIUM IN LIQUID AMMONIA AT −33.5°C.

V_0	Λ	V_0	Λ
0.5047	82,490	30.40	478.5
0.6005	44,100	65.60	540.3
0.6941	23,350	146.0	650.3
0.7861	12,350	318.6	773.4
0.8778	7,224	690.1	869.4
0.9570	4,700	1,551.0	956.6
1.038	3,228	3,479.0	988.6
1.239	2,017	7,651.0	1,009.0
2.798	749	17,260.0	1,016.0
6.305	554.7	37,880.0	1,034.0
13.86	478.3		

centration the conductance rises rapidly. At 2 *N* the conductance has reached the tremendous value of approximately 82,000.

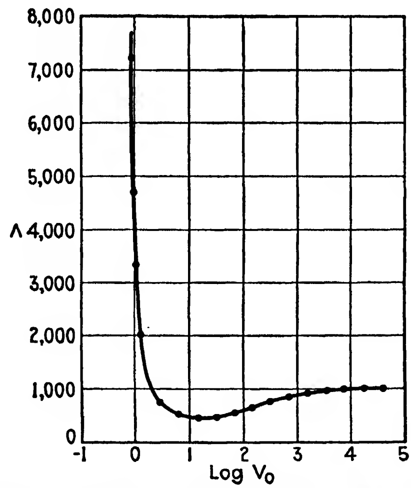

FIG. 3.—Equivalent conductance of sodium in liquid ammonia at −33.5°C.

The change of conductance with change of dilution is shown in Table II and Fig. 3, which are self-explanatory. (The dilution V_0 is expressed in terms of 1,000 cc. of ammonia.)

The extremely high conductance of the concentrated solutions is explained on the assumption that electrons move through the solution in the same way that they move through metals; in other

words, these concentrated solutions of sodium in ammonia exhibit metallic conduction. If this is true, the passage of the electric current would produce none of the material effects in the neighborhood of the electrodes that characterize electrolytic conduction. Cady* has discovered that prolonged electrolysis produces no material effects, the current passes through the liquid ammonia solution without the solution or deposition of any material substance at the electrodes nor is there any change of concentration of the electrolyte in the neighborhood of the electrodes. The electron carries all the current into, out of and through the solution. Furthermore, the specific conductance of the sodium ammonia solution has the same order of magnitude as a metallic conductor such as mercury. Thus we see that liquid ammonia solutions may be considered as a connecting link between metallic and electrolytic conductors; by varying the concentration, the solution can be made to act either as a metal or as an electrolyte, or it can act intermediately between these two extremes.

Hydrogen Fluoride Solutions.—Among the very highly polar liquids that exist in nature must be classed hydrogen fluoride. Hydrogen fluoride has a high dielectric constant, 83.5 at 0°C. and is capable of dissolving a large number of electrolytes. The conductances of a number of salts dissolved in liquid hydrogen fluoride have been measured, but not with a very high degree of accuracy owing to the difficulty in handling hydrogen fluoride. Although we are unable to learn anything of importance in regard to the theory of conductances from these data, nevertheless the results are interesting in that they illustrate the practical applications of conductance measurements to the study of the nature of solutions.†

Table III includes a few examples of the molal conductance of some substances dissolved in hydrogen fluoride at −15°C. as determined by Fredenhagen and Cadenbach.‡

Many important chemical facts can be gleaned from the data in Table III. It will be noticed that water and sulfuric acid have

* Cady, *J. Phys. Chem.*, **1**, 707 (1897).

† See J. H. Simons, *Chem. Rev.*, **8**, 213 (1931).

‡ Fredenhagen and Cadenbach, *Z. physik. Chem.*, **A 146**, 245 (1930); See also Fredenhagen, Cadenbach, and Klatt, *Z. physik. Chem.*, **A 164**, 176 (1933).

TABLE III.—MOLAL CONDUCTANCES OF SUBSTANCES DISSOLVED IN LIQUID HYDROGEN FLUORIDE AT −15°C.
Concentration in Moles per Liter

Substance \ Concn.	0.5	0.24	0.115	0.055	0.026
H_2O	121	153	183	210	228
KF	172	203	225	241	251
AgF	174	201	222	238	247
KNO_3	360	429	482	258	610
$AgNO_3$	390	470			
H_2SO_4	...	151	184	209	232
CH_3OH	139	164	200	225	243
C_2H_5OH	166	180	210	233	246
C_3H_7OH	142	163	196	215	231
$C_5H_{11}OH$	128	158	186	205	222
CH_3COOH	148	175	205	227	241
CCl_3COOH	9	11	11		
C_6H_5COOH	176	181	190	200	226
CH_3COOK	325	367			
CH_3COCH_3	159	182	216	238	252
Glucose	114	165	208	247	279
C_6H_5OH	17	23	31	44	52

identical conductances (within the experimental limits of error). This is explained by the following reactions:

$$H_2O + HF \text{ (the solvent)} = H_3O^+ + F^-$$
$$H_2SO_4 + 2HF \text{ (the solvent)} = HSO_3F + H_3O^+ + F^-.$$

Since water and sulfuric acid react with the solvent to give the same ions, the conductances are identical. Water is assumed to react in the way illustrated, because mixtures of potassium fluoride and water in liquid hydrogen fluoride give conductances that are practically additive. If water did not react with the solvent molecules but dissociated into a proton and a hydroxyl ion, the added fluoride ions from the potassium fluoride would combine with the free proton to give the undissociated solvent molecules and the conductances of water and potassium fluoride would not be additive. The high conductance of potassium nitrate is due to the reaction

$$KNO_3 + 2HF \text{ (the solvent)} = K^+ + H_2NO_3^+ + 2F^-.$$

The conductances of glucose and similar nonelectrolytes (nonelectrolytes when dissolved in water) can be explained on the assumption that these substances act as bases (see Chap. XX for Brønsted's definition of a base as a proton acceptor and acids as proton donors) and accept hydrogen ions or protons from the solvent molecules to form a positive ion and the fluoride ion in the solution:

$$\text{Glucose} + \text{HF (the solvent)} = (\text{H glucose})^+ + \text{F}^-.$$

The data also illustrate the fact that strong acids in water, such as trichloroacetic acid, are weak electrolytes in liquid hydrogen fluoride because they have a small tendency to act as bases. Hydrogen fluoride is the strongest acid known, it must give its proton to other substances; it will not accept protons from anything. Hydrogen chloride is not soluble in liquid hydrogen fluoride.

It would be interesting to test the Onsager conductance equation with data for the hydrogen fluoride solutions, but the experimental technique is yet too far from perfect to warrant any such attempt.

TABLE IV.—PERCENTAGE CHANGE IN Λ WITH VARYING PROPORTIONS OF WATER

Water, %	Methyl alcohol (salt concn. 0.0015 N)			Ethyl alcohol (salt concn. 0.001 N)
	KCl	$AgNO_3$	NEt_4ClO_4	NEt_4ClO_4
¼	−0.4	.....	−0.5	
½	−0.9	−0.6	−1.1	−0.6
1	−2.1	−1.4	.....	−1.3

Acetone (salt concn. 0.001 N)

	NEt_4ClO_4	$HClO_4$	$KCNS$	$AgPic$	$NaCNS$	$AgNO_3$	NH_4CNS	$LiCNS$	$PicOAc$
¼	−0.5	.....	.....	.....	.....	+11.5			
½	−0.8	−1.2	−1.0	+2.2	+3.2	......	+ 8	+35	+250
1	−1.5	−2.4	−2.0	+4.6	+6.0	+48	+15	+65	+550

The Change in Conductance of Nonaqueous Solutions Due to the Addition of Small Amounts of Water.—Hughes and Hartley* have made a systematic study of the effect of adding small amounts of water to solutions of salts in methyl and ethyl alcohol and in acetone. Their results are given in Table IV. The addition of water decreases the equivalent conductance of strong electrolytes but increases the viscosity to a greater extent, so that the product $\Lambda\eta$ increases. The addition of water increases the conductance of weak electrolytes. The increase in the product $\Lambda\eta$ for strong electrolytes is explained by assuming that the ions are smaller in water than in these solvents. The increase in conductance of the weak electrolytes is attributed to an increase in dissociation. Since the values of $\Delta\Lambda$ are proportional to the percentage of water, it is assumed that ion solvation is a statistical process, both the water and alcohol molecules competing for places in the solvent envelope about the ion.

* O. L. Hughes and Sir Harold Hartley, *Phil. Mag.*, **15**, 610 (1933); see also Kolthoff and Willman, *J. Am. Chem. Soc.*, **56**, 1007 (1934).

CHAPTER IX

METHODS OF MEASURING TRANSFERENCE NUMBERS OF SOLUTIONS

Definition.—The migration of chemically different ions through a solution on the passage of an electrical current enables us to determine an important quantity called the transference number. There are three independent methods for measuring the transference number, two of which will be considered in this chapter and the third in a later chapter devoted to galvanic cells.*

We have seen in the previous chapters that the application of an electric field to a solution results in the motion of positive ions in the direction of the negative electrode and negative ions in the direction of the positive electrode. The number of positive ions that migrate to the cathode compared to the number of negative ions that migrate to the anode depends upon the relative velocity of the two kinds of ions. If the velocity of the cation is relatively high as it is in hydrochloric acid, more cations will be transferred in the direction of the cathode than anions in the direction of the anode, and the cations will carry a greater fraction of the total current. The change in concentration which occurs enables us to determine the transference number of an ionic constituent of the electrolyte since the transference number, t_i, may be defined by the equation

$$t_i = \frac{\text{equivalents of ionic constituent transferred}}{\text{equivalents of electricity passed through cell}}. \qquad (1)$$

This definition of transference numbers makes no assumption concerning the manner in which ions are transferred and is based upon no hypotheses concerning the nature of solutions. In the next chapter we shall derive equations for the transference number from considerations concerning the number, nature, and velocity of the ions.

* For a fourth method see R. C. Tolman, *Proc. Am. Acad.*, **46**, 119 (1910).

The Hittorf Transference Number.—In the early days of electrochemistry it was recognized that ions conducted the current through the solution, but it was unknown to what extent each ion participated in the transfer of electricity. Faraday thought that the positive and negative ions carried exactly one-half of the current each, while other scientists believed that all the current was carried by one kind of ion. Thus the whole subject of ion transfer was very puzzling until Hittorf, in the middle of the nineteenth century, carried out his famous experiments that largely solved the problem.

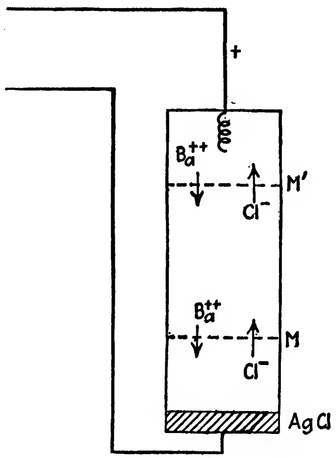

FIG. 1.—Schematic representation of the Hittorf method of measuring transference numbers.

For concreteness let us consider a solution of barium chloride into which are placed two electrodes, the positive electrode or anode being composed of silver and the negative electrode or cathode being composed of silver chloride as represented in Fig. 1.

Let an external source of e.m.f. be applied to the electrodes so that the silver is the anode and the silver chloride is the cathode. As the current flows through the cell, the silver chloride electrode is decomposed, metallic silver being left behind on the electrode while chloride ions enter the solution. The solution in the immediate neighborhood of the cathode, called the **catholyte,** becomes richer in chloride ions due to the electrode process to the extent of one equivalent of chloride per faraday of electricity passed through the cell. But the catholyte does not show a net gain of all this chlorine because chloride ions will be attracted to the anode and will move away from the cathode, thereby tending to lower the chloride ion concentration in the catholyte. In order to determine the final result of these two opposing effects it is necessary to select a definite section of the electrolyte as the catholyte and to consider the concentration changes in this portion of the cell. For this purpose we shall draw an imaginary boundary at M with the stipulation that the distance between M

and the cathode is far enough so that there will be no concentration change at M due to the electrode reaction or to any accidental mixing of the solution at M with the solution near the cathode. In other words, the concentration at M must remain unaltered during the passage of the electrical current.

The electric current which flows by M consists of barium ions flowing in one direction and chloride ions flowing in the other. The transference number of the barium ion is equal to the fraction of the total current carried by the barium ion. If I is the total current and I_+ the current carried by the barium ion, then

$$t_{\mathrm{Ba}} = \frac{I_+}{I}. \tag{2}$$

It is easily proved that Eq. (2) follows from Eq. (1) when it is remembered that current times time divided by the faraday equals the equivalents of electricity or in the case of the ions, equivalents of the ions, *i.e.*,

$$\text{Equivalents of electricity} = \frac{I\tau}{F} \tag{3a}$$

$$\text{Equivalents of the barium ion} = \frac{I_+\tau}{F}, \tag{3b}$$

where τ is the time in seconds. As the current passes through the cell barium ions will migrate into the catholyte so that the catholyte will become richer in barium ions just as it becomes richer in chloride ions from the electrode reaction. The number of equivalents of barium that enter the catholyte will depend upon the magnitude of the current and the duration of the electrolysis. If we let $I\tau/F$ equal s, then by combining Eqs. (2) and (3b) we have for the number of equivalents of barium ion entering the catholyte

$$\frac{I\tau}{F}t_+$$

or

$$t_+s = \text{equivalents of barium entering the catholyte.}$$

At the same time that barium ions are migrating into the catholyte, chloride ions are migrating out of the catholyte; the number of equivalents of chloride leaving the catholyte is given by the equation

$$\frac{I_-\tau}{F} = (I - I_+)\frac{\tau}{F} = s - t_+s.$$

But s equivalents of chloride enter the catholyte from the electrode reaction, so that the total increase of equivalents of chloride in the catholyte is

$$s - (s - t_+s) = t_+s$$

equivalents. The total increase of barium is also t_+s equivalents, and the increase of barium chloride as a whole is t_+s equivalents of the salt, or

$$t_+s = \text{increase of equivalents of barium chloride in catholyte}$$

or

$$t_+ = \frac{\text{equivalents of barium chloride transferred}}{\text{faradays of electricity passed through cell}}, \tag{4}$$

since s is the number of faradays.

It is interesting to compare the phenomena at the anode and in the **anolyte** (the electrolyte about the anode is called the anolyte) with the phenomena that have just been described. At the anode, s equivalents of chloride precipitate on the silver electrode forming silver chloride. Barium ions migrate out of the anolyte to the extent of t_+s equivalents while $(1 - t_+)s$ equivalents of chloride migrate into the anolyte. The change of chloride equivalents is $-s + (1 - t_+)s$ or $-t_+s$ equivalents, while the change of barium is also $-t_+s$ equivalents; the total decrease in barium chloride amounts, therefore, to t_+s equivalents of salt, or

$$t_+s = \text{decrease of equivalents of barium chloride in anolyte},$$

or

$$t_+ = \frac{\text{equivalents of barium chloride transferred}}{\text{faradays of electricity passed through the cell}}. \tag{5}$$

Equation (5) is exactly the same as Eq. (4); hence it is possible to determine the transference number from the concentration changes about either the anode or the cathode or from both.

If the electrodes are not reversible to the chloride ion, but are reversible to the barium ion, the *decrease* in equivalents about the cathode is t_-s and the *increase* in equivalents about the anode is also t_-s. Hence the transference number of the chloride ion is given by the equation

$$t_- = \frac{\text{equivalents of barium chloride transferred}}{\text{faradays of electricity passed through the cell}}.$$

Thus we see that if the electrode reaction concerns the chloride ion solely, the concentration change gives us the transference number of the barium ion, while if the electrode reaction concerns the barium ion, it is the chloride ion transference number that is directly calculated from the data. In the latter case the cathode must be made the top rather than bottom electrode, because the more concentrated solution should be formed at the bottom of the apparatus to avoid convection currents due to density differences.

The definition of transference number as given by Eq. (4) or (5) is perfectly general if only one salt is present, since a transference number can be calculated from an equation like this even if there are complex ions present and if water is also transferred. Transference numbers calculated in this way are called "Hittorf" transference numbers to distinguish them from transference numbers calculated in other ways.

If a mixture of salts is present, the general definition of the Hittorf transference number analogous to Eq. (1) is

$$t_i = \frac{\text{equivalents of the } i\text{th ion transferred}}{\text{faradays of electricity passed through cell}}. \tag{6}$$

In Eq. (6) equivalents of the ith ion refer to the equivalents that are determined analytically.

The Modified Washburn Method for the Determination of Transference Numbers.—The experimental procedure for the determination of the Hittorf transference number as described here is based on the original method of E. W. Washburn.* Jones and Dole† improved his technique somewhat, as did MacInnes and Dole.‡

MacInnes and Dole's modification of the Washburn apparatus is shown in Fig. 2.

The positive electrode is composed of finely divided silver made by smearing silver oxide paste in large quantities onto a silver wire gauze and decomposing it. The negative electrode may be made from precipitated silver chloride or from silver chloride electrolytically deposited upon a silver electrode similar to the anode described above. In fact, the anode of one experiment

* E. W. Washburn, *J. Am. Chem. Soc.*, **31**, 322 (1909).

† Grinnell Jones and M. Dole, *J. Am. Chem. Soc.*, **51**, 1073 (1929).

‡ D. A. MacInnes and M. Dole, *J. Am. Chem. Soc.*, **53**, 1357 (1931).

may be used as the cathode of the next experiment, for during the electrolysis silver chloride is formed on the silver anode. The use of a cathode of this type requires all oxygen to be eliminated from the solution by passing purified nitrogen through the solution before the electrolysis begins. This is to prevent the solution

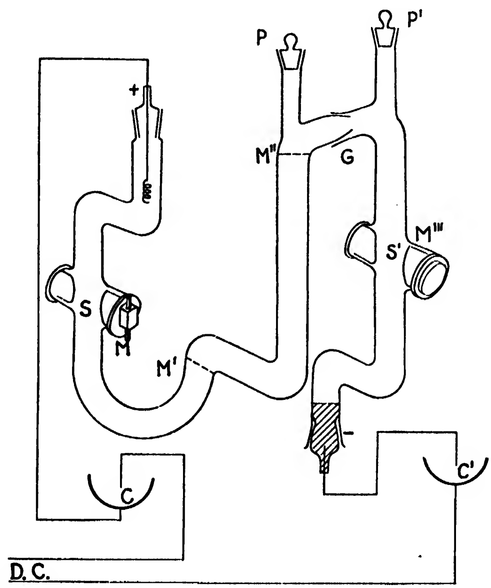

FIG. 2.—The MacInnes and Dole apparatus for the determination of Hittorf transference numbers. The brass key at M is used to turn the stopcocks and is removable.

from becoming alkaline in the catholyte due to the following electrode reaction:

$$O + H_2O + 2\epsilon^- = 2OH^-.$$

The leads to the anode and cathode pass through narrow capillary tubes in the glass stoppers where they can be sealed into place with a cement.

With the electrodes in place, the two halves of the apparatus are connected together at *G* and the whole cell filled with the solution under investigation (necessarily a chloride solution when chloride electrodes are used). The large stopcocks, *S* and *S'*, have the same internal bore as the rest of the apparatus so that there will be no local electrical heating due to a constricted portion

of the solution. If excessive heating occurs, convection currents will be set up tending to cause the anolyte and catholyte to mix with the solution in the middle of the apparatus, thereby spoiling the experiment. The whole apparatus is immersed in a water bath to keep the solution at constant and uniform temperature. MacInnes and Dole also found it advisable to put bends into the apparatus to help break up convection currents.

Two Richards porous cup coulometers measure the faradays of electricity passed through the cell. The duration of the experiment depends upon a number of factors such as current density, concentration of the solution, size of electrodes, etc. The current should be stopped before there is an evolution of gas at either electrode, before there is any mixing of anolyte or catholyte with the middle solution, and before colloidal silver chloride appears at the anode.

When the current is stopped, the large stopcocks, S and S', are immediately turned, separating the anolyte from the middle solution at M and the catholyte from the middle solution at M'''. With a pipet arrangement inserted at P', a portion of the middle solution between M'' and M''', called the cathode middle, is transferred from the cell to a dry weight burette. The solution between M' and M'', called the middle middle, and the solution between M and M', called the anode middle, are likewise transferred to two separate weight burettes. The apparatus is now disconnected at G and the two halves are weighed. The anolyte and catholyte are next transferred to two weight burettes. The electrodes are weighed, and the two halves of the cell, now empty, also are weighed, and from these weighings, the weights of the anolyte and of the catholyte are easily computed. The last part of the experiment is to analyze the five solutions as accurately as possible. If the experiment has been properly performed, the three middle solutions will all analyze to the same percentage composition.

Some typical data obtained by MacInnes and Dole for 0.5c potassium chloride at 25°C. are given in Table I. The concentration of the potassium chloride in the anode middle differs from that of the cathode middle by only 0.03 per cent; thereby indicating that the concentration changes during electrolysis were largely limited to the anolyte and to the catholyte as they should be.

TABLE I.—DATA OBTAINED IN A TRANSFERENCE NUMBER EXPERIMENT ON A 0.5c POTASSIUM CHLORIDE SOLUTION AT 25°C.

Amperes	0.018	KCl transferred out of anolyte (grams)	0.6680
Volts	10	KCl transferred into catholyte	0.6698
Duration of electrolysis (hours)	26	t_K calc. from anolyte data	0.4890
Weight, Ag. in coulometers	1.9769 1.9767	t_K calc. from catholyte data	0.4903
Weight, anolyte	119.48	Average	0.4896
Weight, catholyte	122.93		
% KCl in anolyte	3.1151 3.1151		
% KCl in anode middle	3.6531		
% KCl in middle middle	3.6537		
% KCl in cathode middle	3.6543		
% KCl in catholyte	4.1788 4.1784		

The calculation of the transference number from the observed data is carried out in the following way: Let us consider the catholyte. The weight of the catholyte is the sum of the weights of the potassium chloride and the water. By multiplying the weight of the catholyte by the percentage of potassium chloride as found in the catholyte analysis, the weight of potassium chloride in the catholyte can be computed, and subtracting this weight from the total weight of the catholyte, the weight of water in the catholyte is obtained. This is the weight of water present at the end of the experiment, and it is necessary to assume that the same weight of water was present in the catholyte at the start of the experiment in order to calculate the transference number. In other words the Hittorf transference number is based on the assumption that *the water remains stationary during the electrolysis* and is not transferred either into or out of the anolyte and catholyte. Since there is probably some transfer of water by the ions, the Hittorf transference number does not necessarily agree with theoretical calculations of the transference number.

Having obtained the weight of water in the catholyte, the weight of potassium chloride associated with this weight of water at the beginning of the experiment is obtained by multiplying the weight of water by the ratio,

$$\frac{\%\ \text{KCl in middle middle}}{\%\ \text{water in middle middle}}.$$

The weight of potassium chloride found in the catholyte at the end of the electrolysis minus the weight of potassium chloride in the catholyte at the start of the electrolysis gives the weight of potassium chloride which has migrated into the catholyte during the experiment. This weight of potassium chloride divided by the equivalent weight of potassium chloride gives the equivalents of potassium chloride transferred which divided by the faradays of electricity results finally in the transference number of the potassium ion. In Table II are given some recent data for the transference number.

TABLE II.—TRANSFERENCE NUMBER OF THE CATION AT 25°C.

c	LiCl[a]	KCl[b]	$BaCl_2$[c]
0	0.3337[d]	......	0.4476[d]
0.001	0.3322[d]	......	0.4444[d]
0.002	0.3316[d]		
0.003	0.3311[d]		
0.005	0.3303[d]		
0.01	0.3289[d]	......	0.4375[d]
0.02	0.3269	0.4893	
0.025	......	......	0.4317
0.03	0.3254		
0.05	0.3230	0.4894	0.4253
0.1	0.3187	0.4898	0.4162
0.2	0.3125		
0.25	......	......	0.3986
0.3	0.3079		
0.5	0.3006	0.4896	0.3792
1.0	0.2873	0.4875	0.3528
2.0	0.2690		
3.0	0.2553	0.4857	

[a] GRINNELL JONES and B. C. BRADSHAW, *J. Am. Chem. Soc.*, **54**, 138 (1932).
[b] D. A. MACINNES and M. DOLE, *ibid.*, **53**, 1357 (1931).
[c] GRINNELL JONES and M. DOLE, *ibid.*, **51**, 1073 (1929).
[d] Extrapolated values.

Before taking up the interesting theoretical interpretation of the change of the transference number with the change of concentration let us consider another method for determining the transference number known as the *moving boundary method.*

The Moving Boundary Method.—The moving boundary method for the determination of transference numbers depends

upon principles entirely different from the Hittorf method. As its name implies, the moving boundary method consists in measuring the velocity of motion of a boundary between two solutions, the motion of the boundary being caused by the migration of ions under the force of the applied electric field. This method was chiefly worked out by Denison and Steel,* by MacInnes and his coworkers,† and has recently been brought to a high state of perfection by Longsworth working in MacInnes's laboratory.‡

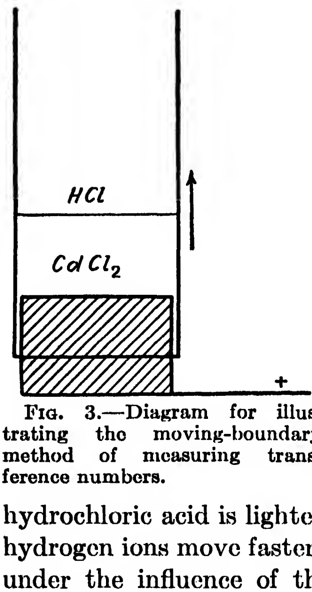

FIG. 3.—Diagram for illustrating the moving-boundary method of measuring transference numbers.

Consider a narrow vertical tube filled with 0.1c hydrochloric acid solution. Sealed into the bottom of the tube is a rod of metallic cadmium (Fig. 3). As the current flows through the cell, cadmium ions will enter the solution if the cadmium electrode is made the anode, and cadmium ions will migrate up the tube. The hydrogen ions of the hydrochloric acid will also move up the tube and will always remain above the cadmium ions since hydrochloric acid is lighter than cadmium chloride and since the hydrogen ions move faster than the cadmium ions when both are under the influence of the same electric force. Although the hydrogen ion has a greater mobility than the cadmium ion, the velocity of the hydrogen and cadmium ions up the tube will be identical because the cadmium ions are acted upon by a greater electrical force than the hydrogen ions. The same total electrical current must flow through both solutions, and since the electrical

* DENISON and STEEL, *Phil. Trans.*, **A 205,** 449 (1906).

† MACINNES and BRIGHTON, *J. Am. Chem. Soc.*, **47,** 994 (1925); MACINNES and SMITH, *ibid.*, **47,** 1009 (1925); MACINNES, COWPERTHWAITE, and BLANCHARD, *ibid.*, **48,** 1909 (1926); MACINNES, COWPERTHWAITE, and HUANG, *ibid.*, **49,** 1710 (1927); MACINNES, COWPERTHWAITE, and SHEDLOVSKY, *ibid.*, **51,** 2671 (1929); MACINNES and COWPERTHWAITE, *Proc. Nat. Acad. Sci.*, **15,** 18 (1929).

‡ CADY and LONGSWORTH, *J. Am. Chem. Soc.*, **51,** 1656 (1929); LONGSWORTH, *ibid.*, **52,** 1897 (1930); **54,** 2741 (1932); MACINNES and LONGSWORTH, *Chem. Rev.*, **11,** 172 (1932).

resistance of the hydrochloric acid is less than the resistance of the cadmium chloride solution, the potential fall per centimeter in the hydrochloric acid is less than in the cadmium chloride solution. This follows from Ohm's law, $I = E/R$. It is also a necessary consequence of the law of electroneutrality of solutions that the cadmium ions keep pace with the hydrogen ions; obviously there can be no appreciable gap between the two kinds of positive ions.

When it is realized that the electric field or the potential gradient is greater in the cadmium chloride solution than in the hydrochloric acid, it is easy to understand why the boundary remains sharp during the passage of the current. If the current were to be stopped, cadmium ions would tend to diffuse into the hydrochloric acid and hydrogen ions would diffuse into the cadmium chloride solution causing the boundary between the solutions to become diffuse and to disappear entirely if given time enough. However, when the external electric field is applied to the solution, the cadmium ions which have diffused into the hydrochloric acid now find themselves in a region of lower potential gradient than do the cadmium ions in the cadmium chloride solution, and as a consequence these diffused cadmium ions will move more slowly and will drop behind the faster moving hydrogen ions until the cadmium chloride solution has overtaken them. Similarly, hydrogen ions which have diffused into the cadmium chloride solution find themselves acted upon by a greater electric force and will consequently speed up until they overtake their own solution. MacInnes and Cowperthwaite* have performed some very interesting experiments to illustrate this point. They stopped the current and allowed two solutions to diffuse together for as long as half an hour. At the end of this period, the current was again allowed to pass and the boundary which had become diffuse reformed and became quite sharp.

From the above discussion it might be concluded that the velocity of the moving boundary is the true velocity of the ions. If this were true, the problem of electrolytic solutions would be well nigh solved since a knowledge of the velocity of the ions

* D. A. MacInnes and I. A. Cowperthwaite, *Proc. Nat. Acad. Sci.*, **15**, 18 (1929).

would lead to exact information concerning the concentration of the ions and the degree of dissociation. But the velocity of the boundary is the velocity of the "ion constituent," to use a phrase of Longsworth's, and not that of the ion itself. If there are present in the hydrochloric acid solution any undissociated hydrogen chloride molecules, they will not move under the influence of the current and will tend to fall back into the advancing cadmium chloride solution. Here, however, the equilibrium

$$HCl \rightleftarrows H^+ + Cl^-$$

is upset due to the absence of hydrogen ions and the hydrogen chloride will, therefore, dissociate. The liberated hydrogen ion then migrates rapidly back to the hydrochloric acid. Thus, the current causes the effective transference of all the hydrogen chloride, whether it be in the form of ions or undissociated molecules, and the velocity measured is the velocity of the acid as a whole. "Ion constituent" refers to the hydrogen ion whether in a free or combined state. This distinction between ionic velocity and ionic constituent velocity has no bearing on the numerical magnitude of the transference number, for it will be shown in Chap. X, in the special case of only two kinds of ions in the solution, that the transference number gives the ratio of the true velocities of the ions independent of the degree of dissociation. The ionic constituent velocity is equal to the true ionic velocity multiplied by the degree of dissociation.

In deriving an equation for transference numbers which can be applied to the moving boundary method it is only necessary to transform the equation defining the Hittorf transference number, Eq. (1), into an equation which contains the quantities measured in a moving boundary experiment, *viz.*, the current I, the time τ, which the boundary takes to sweep through a volume V, and the normal concentration N. The Hittorf transference number is given by the equation

$$t_i = \frac{\text{equivalents of } i\text{th ion transferred}}{\text{equivalents of electricity passed through cell}}. \tag{1}$$

The equivalents of electricity are equal to $I\tau/F$, where F is the faraday. The equivalents of the ith ion transferred are equal

to the volume swept through by the boundary times the concentration VN; hence,

$$t_i = \frac{VNF}{I\tau}. \tag{7}$$

In order to determine V, the volume swept through by the boundary, it is necessary to calibrate the tube represented in Fig. 3 before the experiment. This is done by etching marks on the glass tube in the same manner that a burette or pipet is marked.

The calibration of the volume between certain points is accomplished by weighing the mercury necessary to fill the tube between these marks. By having a number of calibrated points up the tube, it is possible to measure the time that the boundary arrives at each mark and thereby obtain several readings of τ and V which enable several transference numbers of the ion to be calculated from one experiment. The observation of the boundary is made possible by the difference in the refractive indices of the two solutions. As the refractive indices of the two solutions approach each other, the boundary becomes harder to see, and in very dilute solutions the difference in refractive indices is so slight that it is impossible to see the boundary. Sometimes the visibility of the boundary is increased by using a colored ion as the following or "indicating" ion. In this last case the boundary is initially formed between two solutions rather than allowing the boundary to form at the metal electrode. MacInnes and his coworkers used the two solutions method as applied to the falling boundary, and Cady and Longsworth the rising boundary (metal electrode) method. Longsworth has happily combined both methods into one apparatus which will now be described in some detail. Longsworth's apparatus may also be used for experiments in which the boundary falls as well as rises.

The essential parts of Longsworth's apparatus are shown in Fig. 4; the base, frame, and supports of the tubes are omitted as is also the mechanism for turning the glass disks over each other. T and T' are two calibrated and graduated tubes through which the boundary moves. If the experiment is to be carried out with the boundary rising from a cadmium anode, tube T' is used; C is the cadmium electrode sealed in through the heavy glass

disks and G is a silver chloride cathode. To carry out the rising boundary experiment with this apparatus it is only necessary to fill the tube T' with the solution under investigation and to start the current. After a while, the boundary will rise up out of the glass disk, and as it passes the first etched mark, the time is recorded. The time is also recorded as it passes all of the remaining graduations, and from each time taken after the first the transference number can be calculated. The current has to be kept constant during the experiment and must be known. The device for holding the current constant will be described shortly.

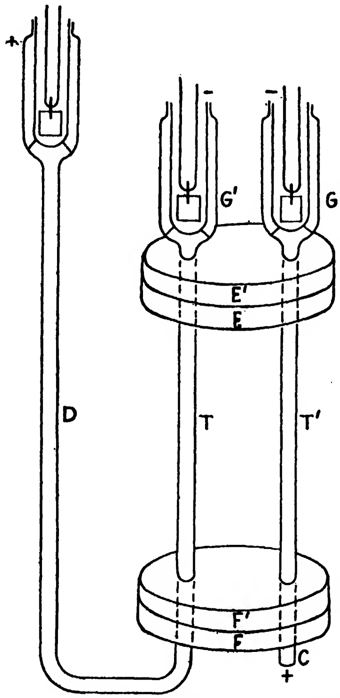

FIG. 4.—Longsworth's moving boundary apparatus.

It is more difficult to establish a sharp boundary between two solutions in a tube than to form the boundary at the metal electrode surface; by means of the shearing mechanism invented by MacInnes and Brighton* which Longsworth incorporated into his apparatus the boundary can be formed with ease. The heavy glass plates, F, F', and E, E' of Fig. 4, are ground so that F and F' and E and E' fit well together and are lubricated lightly so that E' may turn over E and F' over F. If the boundary is to be a rising boundary, the tube D is filled with the following or indicating solution, while T is filled with the solution under investigation. The glass plates E and E' are clamped firmly together and F' is placed upon F in such a position that initially the tube T is not directly over the upturned portion of tube D. The whole apparatus is then placed in a vibration free thermostat and after the solutions have come to temperature equilibrium the necessary potential is applied to the cell. No current will at

* D. A. MacInnes and Brighton, *J. Am. Chem. Soc.*, **47**, 994 (1925).

first flow because there is no direct solution contact between T and D. However, a spring is next released so that the whole apparatus above F turns slowly until the tube T is directly over D; then the current will start flowing and the sharp junction which is formed mechanically between F and F' starts to rise up the tube T. If the boundary is to be a falling boundary, F and F' are clamped tightly together; the solution under investigation is poured into D and also into T up to the top of E. The indicating or following solution is placed in the electrode vessel G' down to the bottom of E'. The top disk E' which carries the electrode vessels G and G' is now placed on E in such a position that G' is not directly over T. As before, the apparatus is placed in a constant temperature bath and after the potential has been applied and temperature equilibrium attained, the disk E' is swung by the spring mechanism around until G' is directly over T. The boundary is now mechanically formed and will proceed to migrate down the tube T.

At this point it is well to consider the conditions which must be fulfilled in order to maintain a sharp boundary and to keep it moving at the proper velocity. The following or indicating solution may not be any solution selected at will, but the concentration of the indicating solution and the transference number of the indicating ion must obey a relationship known as the Kohlrausch* regulating function, *viz.*,

$$\frac{N}{N'} = \frac{t}{t'}. \tag{8}$$

In Eq. (8) N and t refer to the normal concentration and ion transference number of the solution being investigated and N' and t' refer to the normal concentration and ion transference number of the indicating solution.

The Kohlrausch regulating function is based upon the physical necessity of the speed of the leading ion and of the following ion being equal; for example, in the case illustrated in Fig. 3, the cadmium ion, the indicating ion, must proceed up the tube with exactly the same velocity as the hydrogen ion, the leading ion. This will be true only if the Kohlrausch regulating function, Eq. (8), is obeyed. Fortunately in Longsworth's apparatus

* Kohlrausch, *Ann. Physik*, **62**, 209 (1897).

(Fig. 3) the concentration of the cadmium chloride is automatically adjusted to the correct value; but this is not necessarily true in the work of MacInnes and coworkers on falling boundaries. In order to get a proper boundary between two solutions, the concentration of the indicating solution must be adjusted before the start of the electrolysis to the value demanded by Eq. (8). In the case of rising boundaries the concentration of the indicating solution need not be so carefully adjusted as in the case of falling boundaries provided the concentration is in excess of the correct value. The indicating solution in this case acts similarly to the metal anode in adjusting its concentration to the correct value. Falling boundary indicating solutions will not so adjust their concentration, because if they did so, a more concentrated solution would remain behind and on top—but this is a physical impossibility due to the fact that the more concentrated solution has a greater density and could not possibly remain above a more dilute solution.

To illustrate mathematically the principle of the Kohlrausch function, let us start with the mathematical expression that the velocity of the indicating ion $\bar{v}'$ must be equal to the velocity of the leading ion $\bar{v}$, that is

$$\bar{v} = \bar{v}' \tag{9}$$

and

$$u\mathbf{E} = u'\mathbf{E}' \tag{10}$$

where $\mathbf{E}$ is the electric field strength (taken here as a vector quantity) and u is the mobility of the ion. The primes refer to quantities belonging to the indicating solution. Multiplying Eq. (10) by 96,500 (the faraday) and letting Λ_i be the equivalent conductance of the ion (see Chap. IV), we obtain

$$96{,}500u\mathbf{E} = 96{,}500u'\mathbf{E}', \tag{11}$$

or

$$\Lambda_i\mathbf{E} = \Lambda_i'\mathbf{E}'. \tag{12}$$

Ohm's law may be expressed in vector notation (a vector is a quantity having both magnitude and direction) by stating that the vector of the current density $\mathbf{i}$ is equal to the electric field strength times the specific conductance, namely

$$\mathbf{i} = \kappa\mathbf{E}. \tag{13}$$

Substituting the value for **E** given by Eq. (13) into Eq. (12) we obtain

$$\frac{\Lambda_i \mathbf{i}}{\kappa_s} = \frac{\Lambda_i' \mathbf{i}'}{\kappa_s'}. \tag{14}$$

The subscript *s* refers to the specific conductance of the electrolyte as a whole. But $\mathbf{i} = \mathbf{i}'$ and $1/\kappa_s = 1{,}000/N_s\Lambda_s$; hence

$$\frac{\Lambda_i}{N_s\Lambda_s} = \frac{\Lambda_i'}{N_s'\Lambda_s'}. \tag{15}$$

Since the transference number is given by the equation (for a binary electrolyte)

$$t_i = \frac{\Lambda_i}{\Lambda_s},$$

Eq. (15) reduces to the Kohlrausch function, *viz.*,

$$\frac{t_i}{N} = \frac{t_i'}{N'}$$

or

$$\frac{N}{N'} = \frac{t}{t'}. \tag{8}$$

In actual practice it is necessary to carry out a series of experiments in order to determine the correct concentration to use in the indicating solution; this is because the transference numbers are generally not known well enough to calculate the required concentration from Eq. (8). The concentration is first adjusted as nearly as possible by means of Eq. (8) to the correct value.

In the moving boundary method of measuring transference numbers, it is necessary to measure the current accurately and to hold it constant. It is necessary to know the current in order to calculate the transference number from Eq. (7), and it is necessary to hold the current constant in order that the velocity of the boundary up or down the tube will be constant. The measurement of the current is accomplished most readily by measuring the potential drop across a known resistance and then calculating the current from Ohm's law, $I = E/R$. The current can be held constant very accurately by a constant current regulator invented by Longsworth and MacInnes.* Their

* L. G. Longsworth and D. A. MacInnes, *J. Opt. Soc. Am.*, **19**, 50 (1929).

apparatus will not be described in detail here. It consists essentially of a variable rheostat in series with the moving boundary cell. As the total resistance of the cell becomes greater, the resistance of the rheostat is automatically reduced, or if the resistance of the cell decreases, the resistance of the rheostat automatically increases. In this way the total resistance of the entire circuit is kept constant so that under a constant applied voltage the current through the cell remains constant. The variable rheostat can also automatically adjust its resistance if the applied voltage varies, so that it is possible to hold the current through the moving boundary cell constant under conditions of simultaneously varying cell resistance and applied potential.

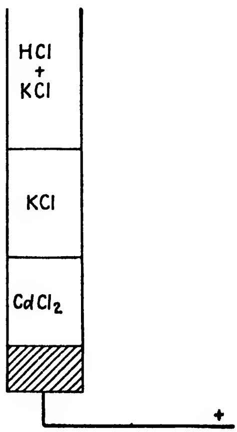

FIG. 5.—Longsworth's moving boundary experiment on the transference numbers of the ions in mixed electrolytes.

The transference numbers as determined by the moving boundary experiment are "Hittorf transference numbers" as G. N. Lewis* pointed out. G. N. Lewis also showed that it is necessary to apply to the observed values a small correction due to volume changes at the electrodes.

It is possible to measure simultaneously the transference numbers of mixtures of electrolytes such as mixed solutions of hydrochloric acid and potassium chloride. In some excellent experiments Longsworth† on electrolyzing a mixture of hydrochloric acid and potassium chloride solution has observed two boundaries rising up his tube. The leading boundary was between the original mixed solution of hydrochloric acid and potassium chloride and a pure solution of potassium chloride and the second boundary was between the potassium chloride solution and the indicating cadmium chloride solution as represented in Fig. 5. From observations of the velocities of the two boundaries the transference numbers of both the potassium and hydrogen ions may be calculated. In this way Longsworth obtained the data quoted in Table III, Chap. VI. Another

* G. N. LEWIS, *J. Am. Chem. Soc.*, **32**, 862 (1910).

† L. G. LONGSWORTH, *J. Am. Chem. Soc.*, **52**, 1897 (1930).

advantage of the moving boundary method is that it enables independent measurements to be made of the transference numbers of both the positive and negative ions.

MacInnes and Dole* have recently shown that results by the Hittorf method and by the moving boundary method agree within the limit of experimental error. Longsworth's data for the moving boundary transference numbers of potassium chloride are compared in Table III with the Hittorf values taken from Table II. Table III also includes other data obtained by Longsworth.

TABLE III.—COMPARISON OF TRANSFERENCE NUMBERS OF POTASSIUM CHLORIDE OBTAINED BY THE HITTORF AND MOVING BOUNDARY METHODS; ALSO OTHER MOVING BOUNDARY DATA (25°C.)

N	0.01	0.02	0.05	0.10	0.20
t_K, Hittorf	......	0.4893	0.4894	0.4898	
t_K, M. B.	0.4903	0.4901	0.4899	0.4898	0.4891
t_{Na}, NaCl	0.3918	0.3902	0.3876	0.3854	0.3814
t_H, HCl	0.8251	0.8266	0.8292	0.8314	
t_{Li}, LiCl	0.3289	0.3261	0.3211	0.3168	

Recently E. R. Smith† has shown that a moving boundary experiment is capable of yielding in a single experiment the change of transference number with change of concentration. If the transference numbers of lithium chloride as given in Table II are examined, it will be noticed that there is a marked change of transference number with change of concentration; the transference number changes from 0.3269 at 0.02c to 0.2553 at 3.0c. Now it was Smith's happy thought to set up a junction between a dilute solution of lithium chloride and a concentrated solution in a moving boundary apparatus. When the current was applied, he found that the boundary moved in an opposite direction to the motion of the positive current. Smith showed the theoretical significance of this to be due to a decrease of transference number with increase of concentration. For lithium chloride solutions between 0.1 and 0.2c Smith found a decrease in transference number of 0.0098 units, which compares favorably with the value

* D. A. MacInnes and M. Dole, *J. Am. Chem. Soc.*, **53**, 1357 (1931).
† E. R. Smith, *Bur. Standards J. of Res.*, **6**, 917 (1931); *ibid.*, **8**, 457 (1932).

of 0.0062 found by Jones and Bradshaw (Table II). In the case of potassium chloride solutions Smith found a slight decrease in the transference number from 0.1 to 1.0*c*, but the motion of the boundary was so slight as to be nearly negligible. In the case of potassium chloride solutions, the correction to be applied to the results due to volume changes at the electrodes amounted to from 50 to 100 per cent of the measured volume change; hence the results are not considered to be very reliable. Between 1.0 and 3.0*c* for potassium chloride Smith found an increase in transference number of 0.0047 compared with the decrease of 0.0018 found by MacInnes and Dole (Table II). However, in this experiment the motion of the boundary continued in the same direction despite the reversal of the current; hence one must conclude that Smith is measuring some effect in addition to the change of transference number with change of concentration.

True Transference Numbers.—As has been stated before, the calculation of the transference number from the Hittorf data involves the assumption that the water remains stationary during the electrolysis. There have been many attempts to determine the motion of the water and to correct the Hittorf transference numbers for this effect. The resulting transference numbers so corrected are called "true transference numbers." The methods used in finding the extent of the migration of the water are generally based on two procedures; one of these procedures consists in adding something to the solution that will remain stationary during the electrolysis, such as nonelectrolytes, like mannite or raffinose, and the second procedure consists in introducing a parchment or another kind of diaphragm into the cell, the diaphragm being supposed to allow ions to pass through but not water. Washburn* has developed the first method and Remy† the second, but it is questionable if either method gives perfectly reliable results. The presence of the raffinose in the solution may upset the state of affairs, and in the second instance it is not at all definite that ions will go through parchment

* E. W. Washburn, *J. Am. Chem. Soc.*, **31**, 322 (1909).

† Remy, *Z. Elektrochem.*, **29**, 365 (1923); Remy and Reisener, *Z. physik. Chem.*, **126**, 161 (1927); Remy, *Trans. Faraday Soc.*, **23**, 387 (1927). See also Buckbock, *Z. physik. Chem.*, **55**, 563 (1906); Ulich, *Trans. Faraday Soc.*, **23**, 392 (1927); Baborovsky and Wagner, *Z. physik. Chem.*, **131**, 129 (1928); **129**, 129, (1927).

unhydrated. The author has discovered* that the hydrogen ion apparently carries water into glass, and if that is true, it is possible that water can be carried by ions through parchment paper. The transfer of water is of appreciable magnitude only in concentrated solutions (because it is only in concentrated solutions that enough ions migrate to transfer much water), and since the exact values of the water transfer are not known definitely, the author will not consider the problem of "true transference numbers" any further here but will be content with the Hittorf numbers whose experimental determination is not open to question.

Exercises

1. Prove that if the electrodes of Fig. 1 are barium electrodes (such as barium amalgam electrodes), the measured concentration changes in both the anolyte and the catholyte give the transference number of the chloride ion.

2. Calculate the transference number of the nitrate ion from the following data obtained in a cell containing silver electrodes and a silver nitrate solution. Weight of silver deposited in coulometer 0.2549 g., weight of anolyte after electrolysis 83.74 g., percentage of silver nitrate in anolyte 5.610, percentage of silver nitrate in middle portion, 5.410.

3. Calculate the transference number from the following data obtained in a moving boundary experiment. Concentration of potassium chloride, 0.9992 N, 0.80 N barium chloride as the indicator solution, current equal to 0.014189 amp., time necessary for the boundary to sweep through a volume of 0.1205 cc., 1675 sec.

4. What should be the concentration of the lithium chloride indicating solution for a 0.1 N potassium chloride solution (at 25°C.)?

5. Assuming no mixing due to evolution of gases, calculate the transference number of the sulfate ion from the following data: sodium sulfate, 0.2 N, electrolyzed at 0.1 amp. for 4 hr., 0.242 g. of sodium sulfate transferred into the cathode portion.

* M. Dole, *J. Am. Chem. Soc.*, **54**, 3095 (1932).

CHAPTER X

THEORETICAL INTERPRETATION OF TRANSFERENCE NUMBERS

The Definition of the Transference Number in Terms of the Velocity of the Ions.—In the last chapter we stated [Eq. (2)] that in the special case of barium chloride the transference number of the barium ion is equal to the current carried by the barium ion divided by the total current flowing through the cell. Let us consider 1 cc. of an electrolyte containing only two kinds of ions. If the voltage drop is 1 v. per centimeter, the current through the 1 cc. is equal to the specific conductance and by Eq. (12) of Chap. V we know that for the positive ion, the specific conductance is equal to

$$\kappa_+ = n_+ q_+ u, \tag{V-12a}$$

and for the negative ion

$$\kappa_- = n_- q_- v. \tag{V-12b}$$

The transference number of the positive ion is, therefore

$$t_+ = \frac{\kappa_+}{\kappa_+ + \kappa_-} = \frac{n_+ q_+ u}{n_+ q_+ u + n_- q_- v}$$

or

$$t_+ = \frac{u}{u + v}, \tag{1}$$

since $n_+ q_+$ must equal $n_- q_-$ in order that the electroneutrality of the solution be maintained. Similarly,

$$t_- = \frac{v}{u + v}. \tag{2}$$

From Eqs. (1) and (2) we obtain the equation

$$t_+ + t_- = 1. \tag{3}$$

It is important to note from Eq. (1) that in this special case of only two kinds of ions present in the solution the transference number depends solely upon the velocity of the ions and is

independent of the degree of dissociation and the stoichiometrical concentration.*

In case there are more than two kinds of ions in solution, the current carried by one ionic constituent will depend not only upon the velocity of the ion but also upon the concentration of the ion. This is easily demonstrated by deriving a general equation for the transference number. The transference number of the ith ion will be given by the equation

$$t_i = \frac{\kappa_i}{\Sigma_i \kappa_i}, \tag{4}$$

where Σ_i means the summation over all kinds of ions. But

$$\kappa_i = \frac{N_i \Lambda_i}{1{,}000} \tag{IV-5}$$

by our definition of the equivalent conductance [Eq. (5) Chap. IV]; hence,

$$t_i = \frac{N_i \Lambda_i}{\Sigma_i N_i \Lambda_i}. \tag{5}$$

Equation (5) is a general equation for the transference number. It might also be written

$$t_i = \frac{N_i u_i}{\Sigma_i N_i u_i}. \tag{6}$$

We also have the relation that

$$\Sigma_i t_i = 1. \tag{7}$$

Classical Interpretation of Transference Numbers.—In developing a theoretical treatment for the explanation of transference numbers, we shall have to content ourselves solely with the problem of explaining the change of transference number with change of concentration. Of the absolute magnitude of the transference number we shall have nothing to say since the relative velocity of an ion at infinite dilution depends upon the effective radius of the ion—a quantity we know nothing definite about. Similarly we shall make no attempt to explain the change of transference number with change of temperature because we

* If the velocities of the ions change with change of concentration, the transference numbers will then depend upon the concentration. See page 155.

know nothing about the change of the ionic radius with change of temperature. There are also no very accurate measurements of the temperature coefficient of transference numbers.

Long before the Arrhenius theory was developed, Hittorf* discovered a change of transference number with change of concentration, small in some cases and very marked in other cases. The greatest change of the transference number with change of concentration is undoubtedly found in the case of cadmium bromide. By the e.m.f. method of determining transference numbers (to be described later) Lucasse† has found that the transference number of the cadmium ion in cadmium bromide varies from a *positive* value of 0.434 at 0.01m to a *negative* value of -0.185 at 3.08m (moles per 1,000 grams water). Hittorf explained this very marked change, which he originally observed, as due to the presence of complex ions. In the case of cadmium bromide the only possible mechanism that would give a negative value is some mechanism that would cause cadmium ions to move backward, that is, toward the positive electrode (the anode). The only way that cadmium can be carried backward is by means of a negative ion that includes cadmium such as $\mathrm{Cd\ Br_3^-}$ or $\mathrm{Cd\ Br_4^=}$. During electrolysis, some cadmium ions will migrate out of the anolyte and will tend to diminish the concentration of the cadmium. But the $\mathrm{Cd\ Br_3^-}$ ion, if present, will migrate into the anolyte, tending to increase the concentration of the cadmium. If $\mathrm{Cd\ Br_3^-}$ is present in large enough concentration, the migration of cadmium out of the anolyte will be more than offset by the migration of cadmium into the anolyte in the form of $\mathrm{Cd\ Br_3^-}$, and the transference number will be less than zero, or negative. It will be remembered that the Hittorf definition of the transference number is

$$t_{\mathrm{Cd}} = \frac{\text{equivalents of cadmium transferred out of anolyte}}{\text{equivalents of electricity passed through cell}}.$$

If there is not net cadmium transferred out of the anolyte, the transference number of the cadmium must be zero or negative. The complex ion theory undoubtedly gives the correct explanation for the concentration gradient of the transference number in cases where this gradient is large, but where the transference

* W. Hittorf, *Pogg. Ann.*, **89**, 177 (1853); **98**, 1; **103**, 1; **106**, 337, 513.
† W. W. Lucasse, *J. Am. Chem. Soc.*, **51**, 2605 (1929).

number changes no more than it does in the data given in Table II, Chap. IX, there is considerable doubt whether the complex ion theory should be applied.

The original theory of Arrhenius predicted transference numbers independent of the concentration since the mobilities of the ions were assumed to remain constant as the concentration was changed. As will be remembered, the degree of dissociation dropped out of the expression for the transference number. But the proponents of the Arrhenius theory had to explain the change of transference number in some way or other; so explanations based on the assumption of complex ions, on the assumption of changes in hydration or water transference of the ions, or on the assumption of a different change in the mobility of the positive and negative ions due to the viscosity change of the medium were proposed. The last explanation can be immediately thrown out, since, as explained in Chap. VI, the mobility of the ions is independent of the viscosity change probably up to a concentration of 0.1*c*. The first two assumptions concerning complex ions and hydration of the ions never led to any quantitative treatment of the transference number change, and for this reason they must be looked upon with considerable suspicion.

The Interionic Attraction Theory of Transference Numbers.—Fortunately, the new Debye modification of the Arrhenius theory provides a logical explanation of the variation of transference number of strong electrolytes with change of concentration.* Shortly after the Debye and Hückel theory was published, Jones and Dole made the interesting discovery that their transference numbers of barium ion in barium chloride solutions (Table II, Chap. IX) could be expressed very accurately up to the high concentration of one molal by the equation,

$$\sqrt{c} = \frac{A}{t_{\mathrm{Ba}} + 1} + B, \tag{8}$$

where A and B are constants.

By plotting $\frac{1}{t+1}$ as ordinates and $\sqrt{c}$ as abscissas a straight line should be obtained if Eq. (8) is valid. In Fig. 1 the values for barium chloride are so plotted, and it is readily seen that the

* E. Hückel, *Erg. d. exakten Naturwissensch.*, **3**, 199 (1924); see also the qualitative remarks by L. Onsager, *Physik. Z.*, **28**, 277 (1927).

experimental results fall on a straight line over the whole concentration range measured.

The actual numerical agreement of Eq. (8) with the data can be tested by selecting the constants A and B to fit the data by

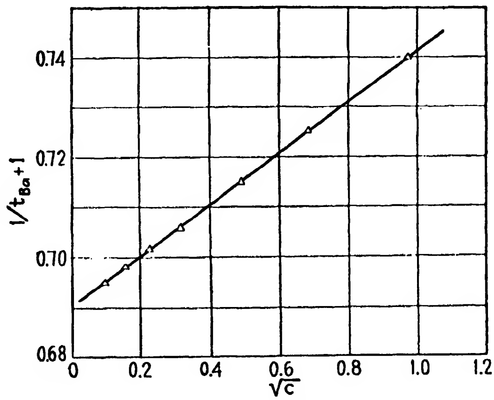

FIG. 1.—The Jones and Dole function for transference numbers.

the method of least squares and then by calculating transference numbers by means of the resulting equation. The equation is

$$\sqrt{c} = \frac{20.6501}{t_{Ba} + 1} - 14.2655,$$

or

$$t_{Ba} = \frac{1.4476}{1 + 0.07010\sqrt{c}} - 1. \tag{9}$$

The calculated and observed values are collected in Table I.

TABLE I.—TEST OF THE JONES AND DOLE TRANSFERENCE NUMBER EQUATION FOR BARIUM CHLORIDE AT 25°C.

c	t_{Ba}, obs.	t_{Ba}, calcd.	Diff., obs.-calcd.
0.0100	0.4378	0.4375	+0.0003
0.02395	0.4315	0.4320	−0.0005
0.04985	0.4252	0.4253	−0.0001
0.05079	0.4250	0.4250	0
0.1003	0.4164	0.4161	+0.0003
0.2475	0.3988	0.3988	0
0.4987	0.3792	0.3793	−0.0001
0.990	0.3530	0.3532	−0.0002
1.035	0.3514	0.3512	+0.0002

The deviations of the theoretical values from the observed are less than the experimental errors. Jones and Bradshaw have shown that the transference number values for lithium chloride (Table II, Chap. IX) also agree with Eq. (8).

Scatchard* proposed an empirical equation for potassium chloride transference numbers before the work of Jones and Dole was published. His equation was of the form

$$t = t_0 - A\sqrt{c}, \tag{10}$$

where t_0 is the transference number at zero concentration and A is a constant. However, Jones and Dole showed that an equation similar to Eq. (10) would not agree with the results for barium chloride transference numbers; hence it is doubtful that Scatchard's equation is the correct function.

It is possible to derive an equation for transference numbers from the limiting equations of the Debye, Hückel, and Onsager theory of conductance. The limiting law for conductance is

$$\Lambda = \Lambda_0 - A\sqrt{c}, \tag{11}$$

where Λ is the equivalent conductance and A is a constant. Equation (11) may also be expressed in terms of the mobility of a simple ion kind, *viz.*,

$$u_i = u_{0,i} - A_i\sqrt{c}. \tag{12}$$

The definition of the transference number [Eq. (1)] of the positive ion of the salt PN is

$$t_p = \frac{u_p}{u_p + u_n}. \tag{13}$$

Substituting the value for the ionic mobility given by Eq. (12) into Eq. (13) and rearranging, one obtains†

$$t_p = \frac{A}{\sqrt{c} - D} + B. \tag{14}$$

In Eq. (14) A, B, and D are all constants, independent of the concentration, and are given by the equations,

* G. Scatchard, *J. Am. Chem. Soc.*, **47**, 696 (1925).

† M. Dole, *J. Phys. Chem.*, **35**, 3647 (1931).

$$A = \frac{A_p u_{0_n} - A_n u_{0_p}}{(A_p + A_n)^2} \tag{15}$$

$$B = \frac{A_p}{A_p + A_n} \tag{16}$$

$$D = \frac{u_{0_p} + u_{0_n}}{A_p + A_n}, \tag{17}$$

where A_p and A_n equal A_i for the positive and negative ion, respectively. Equation (14) may be expressed in a series as follows

$$t_p = B - \frac{A}{D} - \frac{A}{D^2}\sqrt{c} - \frac{Ac}{D^3} \cdot \cdot \cdot \tag{18}$$

Dropping off all terms beyond $\frac{A}{D^2}\sqrt{c}$, Scatchard's Eq. (10) is obtained, since

$$B - \frac{A}{D} = t_0.$$

Thus it is seen that Scatchard's equation is an approximate form of the theoretical transference number equation.

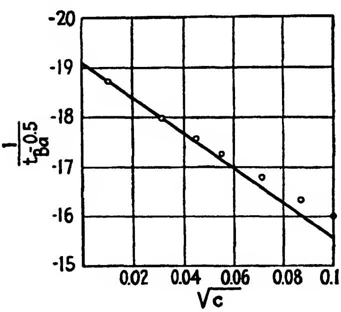

FIG. 2.—Test of the limiting law for the transference number.

By comparing Eqs. (9) and (14) it is readily seen that the Jones and Dole equation has exactly the same form as the theoretical equation, but the constants are different numerically. The B constant for the theoretical equation is usually in the neighborhood of 0.5 while the analogous constant in the Jones and Dole equation is -1.0. One could hardly expect the theoretical equation to be valid in concentrated solutions, for the limiting conductance equations on which it is based are valid only in very dilute solutions. Figure 2 illustrates the agreement between the two Eqs. (9) and (14). The straight line is the limiting law while the circles represent values of the function $1/(t_{Ba} - 0.5)$ calculated from extrapolated transference data [extrapolated by means of Eq. (9)].

Ionic Conductances.—By means of transference number data we are able to calculate ionic conductances. A measurement

of the molal conductance by the methods outlined in Chap. IV gives us the total molal conductance of the solution and not the molal conductance due to either ion kind. The transference number, however, enables us to separate the total molal or equivalent conductances into the ionic molal or equivalent conductances. By Eq. (18), Chap. V, the equivalent conductance of a solute is

$$\Lambda = \alpha F(u + v). \tag{V-18}$$

Similarly we can write for the equivalent conductance of an ion

$$\Lambda_i = \alpha F(u_i). \tag{19}$$

Dividing this latter equation by the former, we have

$$\frac{\Lambda_i}{\Lambda} = \frac{u}{u + v} = t_i,$$

hence,

$$\Lambda_i = t_i\Lambda. \tag{20}$$

Equation (20) is a very useful equation.

According to the Kohlrausch law of the independent migration of the ions (Chap. V), the equivalent conductance of a particular ion at infinite dilution at a definite temperature and in a certain solvent ought to be a constant and independent of its co-ion. Thus, the chloride ion limiting conductance in water at 25°C. ought to be the same whether it is calculated from data obtained from sodium, potassium, barium, etc., chloride solutions. Mathematically,

$$\Lambda_{0,i} = t_{0,i}\Lambda_0 = \text{const.} \tag{21}$$

Equation (21) may be tested by means of the transference data of Longsworth* coupled with the conductance data of Shed-

TABLE II.—THE LIMITING EQUIVALENT CONDUCTANCE OF THE CHLORIDE ION AT 25°C.

Salt	$t_{0,+}$	$t_{0,\mathrm{Cl}}$	Λ_0	$\Lambda_{0,\mathrm{Cl}}$
LiCl	0.3368	0.6632	115.00	76.27
NaCl	0.3963	0.6037	126.42	76.32
KCl	0.4906	0.5094	149.82	76.32
HCl	0.8210	0.1790	426.04	76.26

* L. G. LONGSWORTH, *J. Am. Chem. Soc.*, **54**, 2741 (1932).

lovsky.* These data are collected in Table II with the calculated values for the limiting conductance of the chloride ion. The constancy in $\Lambda_{0,Cl}$ is remarkable considering the uncertainties involved in the extrapolation of the equivalent conductance and the transference number to infinite dilution. MacInnes, Shedlovsky, and Longsworth have also calculated from their data the limiting ionic conductances for a number of other ions, Table III.

TABLE III.—LIMITING IONIC EQUIVALENT CONDUCTANCES AT 25°C. IN WATER

H^+	349.72	Cl^-	76.32
Li^+	38.68	NO_3^-	71.42
Na^+	50.10	CH_3COO^-	40.87
K^+	73.50	OH^-	210.78[a]
Ag^+	61.90	I^-	76.75[b]

[a] G. H. JEFFERY and A. I. VOGEL, *Phil. Mag.*, (7) **15**, 395 (1933); **17**, 582 (1934).
[b] P. A. LASSELLE and J. G. ASTON, *J. Am. Chem. Soc.*, **55**, 3067 (1933).

At finite concentrations the conductance of the chloride ion will depend upon its co-ion, particularly if its co-ion has a valence greater than unity. The data of Table III, Chap. VI, prove that there is a slight variation between the chloride ion conductances in 0.1 N potassium chloride and 0.1 N hydrochloric acid. The Onsager theory does not predict any variation. However, if the positive ion in the chloride solution has a valence greater than unity, the Onsager equation predicts that the conductance of the chloride ion will depend upon both the valence and mobility of the positive ion. The decrease in mobility of the chloride ion with increasing concentration will be greater the greater the valence of its co-ion and the greater the mobility of its co-ion. The dependence of the chloride ion mobility on the valence of its co-ion far outweighs its dependence on the mobility of its co-ion. We have already seen in Table II, Chap. V, that the equivalent conductances of several chlorides decline more rapidly with increasing concentration the higher is the valence of the positive ion. These data do not necessarily prove that the chloride ion conductance decreases more rapidly, but the conductance and transference data for barium chloride solutions, for example,

* T. SHEDLOVSKY, *J. Am. Chem. Soc.*, **54**, 1411 (1932).

obtained by Jones and Dole* show definitely that the chloride ion conductance is considerably less in these solutions than it is in solutions of monovalent salts. At 0.1 N the equivalent conductance of barium chloride is 105.32 while the chloride ion transference number is 0.5747; multiplying these two figures we obtain 60.53 as the chloride ion conductance, which is considerably less than the chloride ion conductance in 0.1 N potassium chloride (65.75).†

Exercises

1. Assuming no interionic attractive forces calculate the specific conductance of a solution 0.5 N in sodium chloride and 1.0 N in hydrochloric acid at 25°C.

2. Derive Eq. (14).

3. Predict the effect on the transference number of the barium ion of increasing numbers of (*a*) $BaCl_3^-$, and (*b*) $BaCl^+$, with increasing concentration.

4. Calculate the mobility of the chloride ion in 0.1 N lanthanum chloride at 25°C. and compare this mobility with the mobility of the chloride ion in 0.1 N potassium and barium chlorides. Find the necessary data in the literature.

* Grinnell Jones and M. Dole, *J. Am. Chem. Soc.*, **51**, 1073 (1929); **52**, 2245 (1930).

† Transference numbers in mixed aqueous solutions of alkali chlorides have been determined by a number of workers for the purpose of investigating the possible existence of complex ions. It is found that the experimental data can be interpreted without the necessity of assuming the existence of complex ions. For the latest results and bibliography see P. Van Rysselberghe, *J. Am. Chem. Soc.*, **55**, 990 (1933); P. Van Rysselberghe and L. Nutting, *ibid.*, **55**, 996 (1933). Hammett and Lowenheim, *J. Am. Chem. Soc.* **56**, 2620 (1934), have shown in a paper which appeared after this text had gone to press that transference number data for the barium ion in barium bisulfate solutions having sulfuric acid as the solvent indicate that the greater part of the conduction in this solvent is due to proton jumps (see the theory of Bernal and Fowler, Chap. XXIX). The transference number of barium ion is only 0.0100 or less.

CHAPTER XI

METHODS OF MEASURING THE DIELECTRIC CONSTANT

Definitions.—The measurement of the dielectric constant of substances and the interpretation of the results in terms of molecular structure have recently constituted a major development in the field of electrochemistry. The experimental technique for the measurement of the dielectric constant by the most common methods is based on many of the principles on which conductance measurements are based; for this reason we shall consider dielectric constants at this point.

The dielectric constant D is defined by Coulomb's law. The force f that exists between two particles *in vacuo* having the charges q_1 and q_2 and separated by a distance r is given by the equation

$$f = \frac{q_1 q_2}{r^2}. \tag{1}$$

If the charges are not separated by a vacuum but by a material medium, the force between the charges is reduced as was first discovered by Faraday. To allow for this fact we must introduce into Coulomb's law a factor $1/D$, which will measure the extent to which the material medium reduces the force between the two charges; thus

$$f = \frac{q_1 q_2}{D r^2}, \tag{2}$$

where D is the dielectric constant. The dielectric constant of a vacuum is by definition equal to unity while the dielectric constant of any other medium is greater than unity. By measuring the force between two charged bodies when they are separated by a vacuum and when they are separated by a material medium, the dielectric constant can be determined.

The dielectric constant is most frequently measured, however, by comparing **capacitances.** The capacitance of a condenser is directly proportional to the inductive capacity, or dielectric

constant, of the medium between the condenser plates. If the capacitance of a condenser is first measured with a vacuum separating the plates and then measured with a material medium separating the plates, the ratio of the latter measurement to that of the former gives the dielectric constant, or

$$\frac{C}{C_0} = D, \tag{3}$$

where C_0 is the capacitance of the condenser *in vacuo* and C is the capacitance of the condenser with a medium of dielectric constant D between the plates.*

The total charge Q which will flow into a condenser is directly proportional to the capacitance of the condenser and to the impressed voltage E. Mathematically speaking,

$$Q = CE. \tag{4}$$

The practical international unit of capacitance is called the **farad** (in honor of Faraday); the capacitance of a condenser may be calculated in farad units from Eq. (4) if Q is expressed in coulombs and E in volts. The farad, however, is not a convenient unit as it is far too large; thus, the capacitance of the whole earth is only a small part of a farad. The customary unit of capacitance is the microfarad which is one-millionth part of a farad. Small capacitances may even be expressed in units of a millimicrofarad or of a micromicrofarad. The relationship between these units can be expressed by the equation

$$1 \text{ farad} = 10^6 \text{ microfarads} = 10^9 \text{ millimicrofarads} = 10^{12} \text{ micromicrofarads.}$$

If three capacitances, C_1, C_2, C_3, are connected in series, the total capacitance C is given by the equation

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} + \frac{1}{C_3} \tag{5}$$

* In his electromagnetic theory of light, Maxwell derived the relationship $n = \sqrt{D}$, where n is the refractive index of a substance having a dielectric constant D and a magnetic permeability equal to unity. Both D and n must be measured at the same wavelength of light and of alternating current. For polar liquids such as water the dielectric constant decreases with increasing frequency. This effect, known as anomalous dispersion, is due to the inability of the polar molecules to orient themselves in a rapidly alternating electric field.

while a parallel arrangement of the capacitances gives for the total capacitance

$$C = C_1 + C_2 + C_3. \tag{6}$$

The capacitance of a parallel-plate condenser is given by the equation

$$C = \frac{DA}{4\pi r}, \tag{7}$$

where D is the dielectric constant of the medium between the plates, A the area of one of the plates, and r the distance between them. This equation is based on the assumption that r is small in comparison to the length and width of the plates. If A is measured in square centimeters and r in centimeters, Eq. (7) becomes

$$C = 0.0885 \times 10^{-6}\frac{DA}{r} \text{ microfarad.} \tag{8}$$

As mentioned above, the dielectric constant is usually measured by comparing capacitances. Capacitances may be compared by two methods, the Wheatstone bridge method and the heterodyne beat method. We shall consider first the alternating-current Wheatstone capacitance bridge.

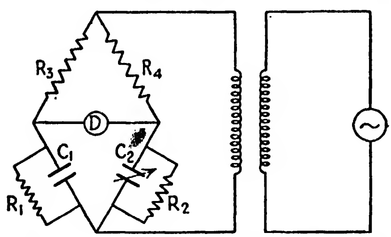

FIG. 1.—An alternating-current Wheatstone bridge for the comparison of capacitances.

The Wheatstone Bridge Method for the Measurement of the Dielectric Constant.—Direct current or alternating current may be employed in the comparison of capacitances by means of the Wheatstone bridge. In Fig. 1 there is represented an alternating-current capacitance bridge. Let us assume at first that the capacitances C_1 and C_2 are perfect; that is, their direct-current resistance is infinite. This means that we may consider R_1 and R_2 to be nonexistent. At balance the impedance of all four arms of the bridge must fulfill the relationship

$$\frac{Z_1}{Z_2} = \frac{Z_3}{Z_4}. \tag{9}$$

If the resistances are perfect resistances,

$$R_3 = Z_3 \quad \text{and} \quad R_4 = Z_4, \tag{10}$$

furthermore,

$$Z_1 = \frac{1}{j\omega C_1} \tag{11}$$

and

$$Z_2 = \frac{1}{j\omega C_2}$$

(see Chap. IV); hence

$$\frac{R_3}{R_4} = \frac{C_2}{C_1}. \tag{12}$$

The capacitances, therefore, are inversely proportional to the resistances.

Actually it is never possible to obtain a perfect condenser; every condenser "leaks" to some extent; that is, every practical condenser has some direct-current conductivity. A leaky condenser may be represented as in Fig. 1 with the resistances, R_1 and R_2 in parallel with the capacitances C_1 and C_2. If energy losses are present in arms 1 and 2 of the bridge (which is the same thing as saying that the condensers are leaky), the current flowing in arm 3 will not be in phase with the current in arm 4 (*i.e.*, the potential across 3 will not always be equal to the potential across 4 at the same time); and it will be impossible to obtain a sharp balance of the bridge. If a telephone is used as the detector D of Fig. 1, there will be a considerable range of adjustment over which the sound is faint, but never entirely disappears. This means that it is necessary to balance the resistances R_1 and R_2 just as it is necessary to balance the capacitances. In our study of conductance measurements, we found that it was necessary to introduce into the bridge a variable condenser in order to balance the unavoidable capacitance inherent in the conductance cell. In the measurement of capacitance, it is necessary to introduce a variable resistance to balance the unavoidable energy losses of the condensers.

There is also another method of reducing the difficulties due to a leaky condenser, and that is to increase the frequency of alternations of the alternating current. The impedance of a pure resistance and capacitance connected in parallel (R_1 and C_1 in Fig. 1, for example) is given by the equation

$$Z = \frac{1}{\frac{1}{R} + j\omega C}. \tag{13}$$

By increasing ω, the term $j\omega C$ becomes large in respect to $1/R$, and $1/R$ can be neglected. By decreasing ω, the term $1/R$ becomes predominant. Hence capacitance measurements are made with high-frequency alternating current while resistance measurements are made with low-frequency alternating current. It is not possible to increase the frequency indefinitely in capacitance measurements, however, because a new error due to inductance in the leads becomes of importance at very high frequencies. A third method of balancing the energy losses in the arms 1 and 2 is to introduce small series resistances into the two arms instead of large parallel resistances. This method has been employed by Smyth, Morgan, and Boyce.* The vacuum-tube oscillator used by Smyth, Morgan, and Boyce generated alternating current having a frequency of 500,000 cycles per second. They used a substitution method of measuring the capacitance of the unknown cell; that is, they first adjusted their bridge to balance without the unknown capacitance connected. Then they connected the unknown capacitance in parallel with their precision variable condenser, such as C_2, of Fig. 1. The decrease in the capacitance of the standard condenser necessary to restore the total capacitance to its original value gives immediately the capacitance of the unknown. The unknown condenser is first filled with air and then with the liquid under investigation. The ratio of the second measurement to that of the first should give the dielectric constant of the liquid, but there is a slight error involved in this procedure. There is an unavoidable capacitance between the leads to the condenser, and the air dielectric of this additional capacitance does not get filled with liquid when the air is replaced by liquid in the main part of the condenser. Hence, if the original capacity measurement is $C_0 - C_x$, the second measurement is $C - C_x$; the dielectric constant is then given by the equation

$$C - C_x = D(C_0 - C_x) \tag{14}$$

and it is impossible to calculate D because C_x, the capacity between the leads, cannot be eliminated from the equation. Methods of getting around this difficulty are either to calculate C_x from the geometrical construction of the leads or to use a

* SMYTH, MORGAN, and BOYCE, *J. Am. Chem. Soc.*, **50**, 1536 (1928).

method of differences invented by Williams and Krchma.* Their condenser containing the unknown is a variable condenser so that two or more readings at different capacitance values may be taken with the condenser filled with air and with the unknown liquid.

Since C_x is the same for all readings, it is eliminated in the final calculation as demonstrated in Eq. (15):

$$(C'' - C_x) - (C' - C_x) = D(C_0'' - C_x) - (C_0' - C_x) \quad (15)$$

when the double and single primes refer to the second and first settings of the unknown condenser.

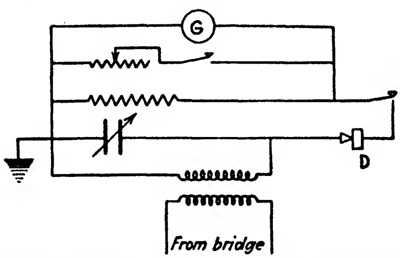

FIG. 2.—Detector of the capacitance bridge used by Smyth, Morgan, and Boyce.

In the use of high-frequency currents it must be remembered that the human ear cannot hear sound of frequency much above 10,000 cycles per second. For this reason the detector D of the apparatus illustrated in Fig. 1 cannot be simply a telephone. Smyth, Morgan and Boyce's detector arrangement is illustrated in Fig. 2. Current from the bridge proper is picked up by the detector circuit through induction. G is a Leeds and Northrup high-sensitivity galvanometer which serves to detect any current flowing in the detector circuit. Of course, the current induced in the detector circuit is alternating current which would have no effect on the galvanometer were it not for the fact that the crystal detector D rectifies the current in the galvanometer circuit. Minimum deflection of the galvanometer indicates that the bridge is in balance. The bridge, oscillator, and detector circuits were properly screened.

The Heterodyne Beat Method for the Measurement of the Dielectric Constant.—Another important method for the deter-

* WILLIAMS and KRCHMA, *J. Am. Chem. Soc.*, **48**, 1888 (1926).

mination of the dielectric constant is the heterodyne beat method. As we saw in Chap. IV, the frequency of oscillations produced by the vacuum-tube oscillator depends upon the inductance and capacitance of the oscillator circuits. Imagine two such oscillating circuits, the first giving current having a frequency of 1,001,000 cycles per second and the second oscillator giving a current having a frequency of 1,000,000 cycles per second. The difference between the two is 1,000 cycles per second, called *beats*, which can be heard in a telephone if the telephone circuit is loosely coupled to the two oscillators. The principle of this phenomenon is illustrated in Fig. 3: The current

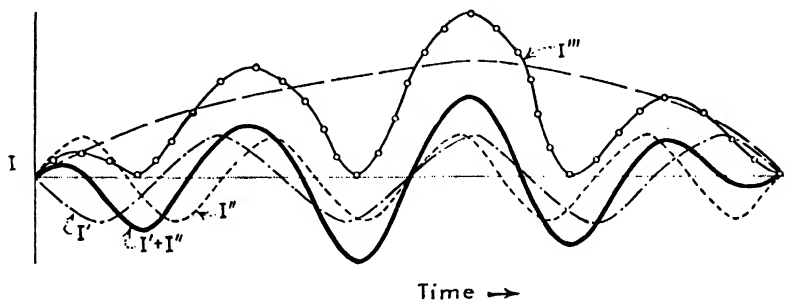

Fig. 3.

is plotted against the time (total time is 1 sec.) for several frequencies; I'', the dotted line, represents a current having a frequency of 4 cycles per second, I', the dashed line, a frequency of 3 cycles per second and $I' - I''$, the solid line, the resultant of the two currents which is picked up in the telephone circuit. The amplifier circuit rectifies the current, I''' is the rectified current, so that what one hears in the telephone is sound represented by the long-dashed line on top which has a frequency of one cycle per second, the difference between 4 and 3 cycles per second.

The heterodyne beat apparatus as used by Williams* after a few modifications by Smyth is illustrated in Fig. 4. The technique of operation is as follows: if oscillator I is so adjusted as to give a frequency of 1,001,000 cycles and oscillator II a frequency of 1,000,000 cycles, the telephone will hear a beat of 1,000 cycles. By turning the precision condenser in circuit I it is possible to

* J. W. Williams, *J. Am. Chem. Soc.*, **52**, 1831 (1930).

increase the capacitance and thereby to decrease the frequency. As the frequency decreases from 1,001,000 cycles, the tone in the telephone becomes lower and when the frequency is exactly 1,000,000 cycles, there is complete silence in the telephone. If the capacitance of circuit I is raised still higher, the frequency will drop below 1,000,000 cycles and the note in the telephone will be

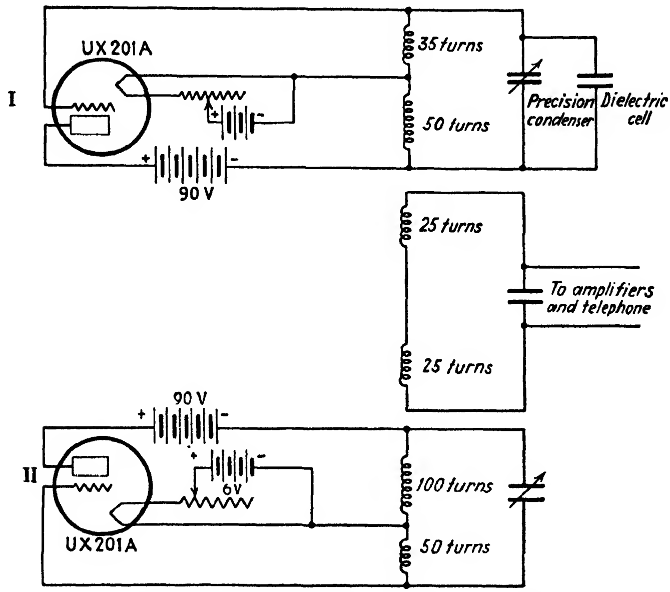

FIG. 4.—Heterodyne beat apparatus for determination of the dielectric constant.

heard again. As the frequency becomes still lower, the pitch of the note in the telephone rises, and eventually will become too high for the human ear to hear. But because of the minimum in the note heard it is possible to adjust circuit I so that the frequency of the current generated by it is equal to the frequency of the standard circuit II. This means that it is possible to adjust circuit I so that its total capacitance is always the same. After the original adjustment, the dielectric cell is introduced, and the decrease in the capacitance to its original value gives the capacitance of the dielectric cell.*

* Wyman, *Phys. Rev.*, **35**, 623 (1930), has devised an interesting dielectric constant measurement method which avoids the uncertainty due to induction effects in the leads. He immerses within the liquid whose dielectric

Smyth* has summed up the relative advantages of these different methods as follows: "It may be said that, for gases, the heterodyne beat method is by far the best, for liquids of negligible conductivity, the beat method is the simplest and most convenient means of making an accurate measurement, while, for liquids of appreciable but not large conductivity, the bridge method is useful. The simplicity of operation and general applicability are great advantages of the bridge, although it is not capable of as great accuracy as the beat method. . . . No method has, as yet, proved accurate and wholly satisfactory for highly conducting liquids." The question of the dielectric constant of conducting liquids is of interest in regard to the Debye theory of solutions. Astin† has recently reviewed the data for the dielectric constant of aqueous solutions as obtained by a number of investigators, and finds that no two methods agree. Wien,‡ on the other hand, in a more recent paper describes measurements of the dielectric constant of electrolytic solutions using very high-frequency currents and finds that the dielectric constant increases with the concentration as predicted

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constant is desired a small circular metallic resonator. Since the resonator is a system containing resistance, inductance, and capacitance in series and since its capacitance depends upon the dielectric constant of the medium in which it is immersed, it is possible to calculate the dielectric constant if the frequency at resonance is known. The frequency is determined by measuring the frequency of an oscillating circuit when the latter is coupled to the metallic resonator, the point of resonance being indicated by a sharp rise in the plate current of the vacuum tube of the oscillating system. Frequencies for every setting of the variable oscillating circuit were obtained by comparison with the frequencies of oscillation of a quartz crystal. The dielectric constant of the liquid is given by the equation

$$D = \frac{f_0^2}{f^2}, \tag{16}$$

where f_0 is the frequency when the resonator is placed in air and f the frequency when the resonator is placed in the liquid. This paper of Wyman's contains an interesting discussion of other methods of measuring the dielectric constant.

* C. P. Smyth, *loc. cit.*

† Allen Astin, *Phys. Rev.*, **34**, 300 (1929); see also Malone, Ferguson, and Case, *J. Chem. Phys.*, **1**, 836, 842 (1933).

‡ M. Wien, *Ann. Physik*, (5) **11**, 429 (1931). See also P. Wenk, *Ann. Physik*, **17**, 679 (1933).

by Debye and Falkenhagen.* Although Wien's results seem reliable, they do not give the dielectric constant directly, inasmuch as the very high frequencies cause a dispersion (change of dielectric constant with change of frequency) of the dielectric constant.†

Exercises

1. Derive the relations: (*a*) For capacitances connected in series:

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} + \frac{1}{C_3} \cdot \cdot \cdot$$

(*b*) For capacitances connected in parallel:

$$C = C_1 + C_2 + C_3 \cdot \cdot \cdot$$

2. Calculate the capacitance of a parallel-plate air condenser whose plates are 10 cm. on a side and are 0.1 cm. apart.

3. How many coulombs will flow into the condenser of Exercise 2 if the impressed voltage is equal to 10 mv? How many electrons is this?

4. The capacitance of an isolated sphere in c.g.s. electrostatic units is given by the equation,

$$C = r,$$

where r is the radius. Calculate the capacitance of the earth. One c.g.s. electromagnetic unit of capacity is equal to 10^9 farads and is equal to c^2 c.g.s. electrostatic units of capacity, where c is the velocity of light. The diameter of the earth is approximately 6×10^6 meters.

5. How many electrons per square meter must strike the earth in order to lower the earth's potential 1 v.?

6. Derive Eq. (16).

* See H. Falkenhagen, *Rev. Mod. Phys.*, **3**, 420 (1931).

† P. Debye and H. Falkenhagen, *Physik. Z.*, **29**, 401 (1928).

CHAPTER XII

DIELECTRIC CONSTANTS AND ELECTRIC MOMENTS

The Clausius and Mosotti Equation.—We are chiefly interested in dielectric-constant measurements because through the equation of Clausius and Mosotti and through the equation of Debye we are able to relate these measurements to quantities characteristic of the individual molecules, thereby obtaining valuable information concerning the structure and electrical nature of both inorganic and organic substances. It is to be expected that measurements of the dielectric constant when properly interpreted will give us information concerning the molecule inasmuch

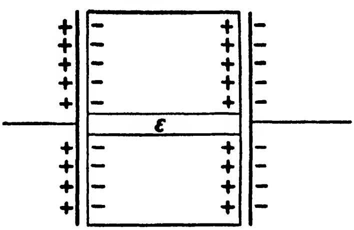


FIG. 1.

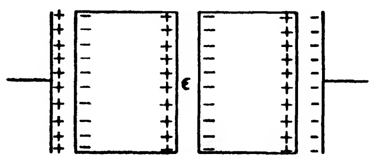


FIG. 2.

as a dielectric is sometimes defined as a body in which electrons cannot move outside of the molecules in which they are contained.*

In order to derive the Clausius and Mosotti relation and to understand the connection between the dielectric constant and the structure of molecules, it is necessary to introduce several new quantities and concepts. Imagine a unit electric charge placed in a dielectric between two condenser plates. If the unit charge is placed in a narrow cylindrical cavity cut parallel to the lines of force as in Fig. 1, the force acting on the charge is called the **electric intensity, E,** and is less than the force which would be exerted on the charge if the medium of the dielectric were a vacuum due to the fact that charges are induced on the faces of the dielectric opposite the plates, charges which produce a force

* N. R. CAMPBELL, "Modern Electrical Theory," p. 32, Cambridge, 1913.

in the opposite direction to the force produced by the charges on the plates of the condenser. If the unit charge is placed in a cavity between two planes very near to each other and perpendicular to the lines of force as in Fig. 2, the force acting on the charge is called the **electric displacement, G.*** (In this derivation we shall make use of vector quantities denoted by **bold-faced** symbols.) The electric displacement is greater than the electric intensity due to the charges induced on the surface of the cavity which produce a force having the same direction as the force due to the charges on the plates. Actually the force **G** is equal to the force which the charges on the plates alone would exert or is equal to **E** when the medium between the plates is a vacuum. The dielectric constant in terms of **G** and **E** is given by the equation

$$\mathbf{G} = D\mathbf{E}. \tag{1}$$

By Gauss's theorem† the force due to the charges on the plates is $4\pi\sigma(\mathbf{n})$ where σ is the surface density of charge and $\mathbf{n}$ is a unit vector perpendicular to the plane of the plates; hence

$$\mathbf{G} = 4\pi\sigma(\mathbf{n}) \tag{2}$$

regardless of the nature of the dielectric.

The magnitude of the force **E** depends upon the number of induced charges on the faces of the dielectric facing the two plates of the condenser and the number of induced charges depends upon the ease with which the dielectric can be polarized or, in other words, upon the polarizability of the dielectric. The **electric moment m** which can be induced in a substance by an applied electric field is equal to the distance **r** by which the two charges, $+q$ and $-q$, are separated, multiplied by the charge, or

$$\mathbf{m} = q\mathbf{r}. \tag{3}$$

* For a description of these forces and a derivation of the Clausius and Mosotti equation see P. Debye, "Polar Molecules," Chap. I, Chemical Catalog Company, Inc., New York, 1929. Also C. P. Smyth "Dielectric Constant and Molecular Structure," Chemical Catalog Company, Inc., Chap. I, New York, 1931.

† Gauss's theorem states that the number of lines of force cutting a surface is equal to $4\pi q$, where q is the total charge enclosed by the surface.

The farther the charges are separated by the applied field, the greater is the moment. It is possible, however, that a molecule may possess an electric moment of its own; that is, the molecule may have a **permanent electric moment** μ which exists in the absence of an applied electric field. Molecules which possess permanent electric moments are called **polar molecules,** while substances not possessing permanent electric moments are called **nonpolar.** All substances (except those that conduct too well) may have temporary electric moments induced in them by an applied field, but it is the determination of the magnitude of the permanent electric moment μ that will interest us chiefly in this chapter. At this point we shall consider only the temporary moment, **m**; in the derivation of the Debye equation we shall return to a discussion of the permanent moment. The electric moment per unit volume, **I**, is equal to $n\mathbf{m}$, where n is the number of electric dipoles per unit volume. The force on the unit charge placed in the dielectric as pictured in Fig. 1 can now be written down. As before, the force due to the charges on the plates is $4\pi\sigma(\mathbf{n})$; the force due to the induced charges is $4\pi\mathbf{I}$ which also follows from Gauss's law; the resulting force, **E**, is given by the equation

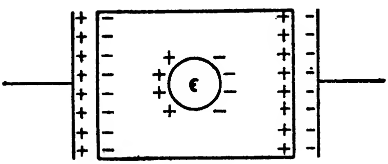


Fig. 3.

$$\mathbf{E} = 4\pi\sigma(\mathbf{n}) - 4\pi\mathbf{I}. \tag{4}$$

Combining Eqs. (2) and (4) we have

$$\mathbf{G} = \mathbf{E} + 4\pi\mathbf{I}. \tag{5}$$

Let us now consider a single molecule placed in an electric field. If the **actual electric intensity** acting on the molecule is **F**, an electric moment $\alpha_0\mathbf{F}$ will be induced in the molecule, or

$$\mathbf{m} = \alpha_0\mathbf{F}, \tag{6}$$

where α_0 is defined as the **polarizability.** The temporary electric moment is thus seen to be directly proportional to the force **F** and to the polarizability of the molecule. For any particular molecular species, α_0 should be a constant. The actual electric intensity **F** is different from either **E** or **G** as can be demonstrated by considering a unit charge placed in a very small spherical cavity scooped out of the dielectric as in Fig. 3. The force **F** can

be considered as being the sum of three forces, $\mathbf{F}_1$, $\mathbf{F}_2$, and $\mathbf{F}_3$. $\mathbf{F}_1$ is the force due to the charges on the plates and is equal to $4\pi\sigma(\mathbf{n})$. $\mathbf{F}_2$ is the force due to the charges induced on the surfaces of the dielectric facing the plates and on the surface of the cavity and is equal to $-4\pi\mathbf{I} + \frac{4}{3}\pi\mathbf{I}$. $\mathbf{F}_3$ is the force due to other molecules which may be in the cavity, but this force may be assumed to be negligible. We have then for $\mathbf{F}$,

$$\mathbf{F} = 4\pi\sigma(\mathbf{n}) - 4\pi\mathbf{I} + \frac{4}{3}\pi\mathbf{I}, \tag{7}$$

and by combining Eqs. (4) and (7)

$$\mathbf{F} = \mathbf{E} + \frac{4}{3}\pi\mathbf{I}. \tag{8}$$

The Clausius and Mosotti equation may be easily derived by making use of the above relations. The electric moment per unit volume, $\mathbf{I}$, is given by the equations

$$\mathbf{I} = n\mathbf{m} = n\alpha_0\mathbf{F} = n\alpha_0(\mathbf{E} + \frac{4}{3}\pi\mathbf{I}), \tag{9}$$

where n is now the number of molecules per unit volume. From Eq. (5) we have

$$\mathbf{I} = \frac{\mathbf{G} - \mathbf{E}}{4\pi},$$

hence

$$\mathbf{G}(1 - \frac{4}{3}\pi n\alpha_0) = \mathbf{E}(1 + \frac{8}{3}\pi n\alpha_0). \tag{10}$$

The dielectric constant is defined by Eq. (1)

$$\mathbf{G} = D\mathbf{E};$$

therefore Eq. (10) becomes

$$\frac{D - 1}{D + 2} = \frac{4\pi n\alpha_0}{3}, \tag{11}$$

which is the Clausius and Mosotti relation. If $\mathbf{N}$ is Avogadro's number, d the density, and M the molecular weight of the substance under consideration, n is equal to $\mathbf{N}d/M$ and

$$\frac{D - 1}{D + 2}\frac{M}{d} = \frac{4\pi}{3}\mathbf{N}\alpha_0 \equiv P_0, \tag{12}$$

where P_0 is the polarization per mole. Both P_0 and α_0 have the dimensions of volume.

From Eq. (12) it is evident that the molal polarization should be independent of temperature if the derivation of Clausius and

Mosotti is correct. This is true for a number of liquids and gases, but in many cases it is very far from being true. The molal polarization of two liquids which conform to Eq. (12) and of two gases which do not conform to it are given in Table I.*

TABLE I.—TEMPERATURE DEPENDENCE OF THE MOLAL POLARIZATION

t, °C.	P(cc.) C_8H_{18}[a]	P(cc.) C_6H_6	t °C.	P(cc.) NH_3	t, °C.	P(cc.) $CH_3COOC_2H_5$
−90	39.19	.....	19.1	57.57	29.1	88.0
−70	39.27	.....	35.9	55.01	53.5	83.2
−50	39.32	.....	59.9	51.22	76.2	79.5
−30	39.37	.....	113.9	44.99	106.4	75.0
−10	39.40	.....	139.9	42.51	193.5	65.6
10	39.43	26.73	172.9	39.59		
30	39.44	26.80				
50	39.46	26.82				
70	39.58	26.80				

[a] 2, 2, 4-trimethylpentane.

In the case of the two hydrocarbons listed it is evident that the theoretical treatment of Clausius and Mosotti provides an adequate explanation for the observed dielectric constant data, but in the case of ammonia and ethyl acetate it appears necessary to introduce into Eq. (12) a term which is a function of temperature. The data clearly prove that we must invent some concept which will explain the decrease in the molal polarization as the temperature is increased.

Debye's Equation.—It will be remembered that the Clausius and Mosotti expression was derived on the assumption that the molecules of the dielectric possessed no permanent electric moment of their own, but that they acquired an electric moment only in the presence of an applied electric field. However, there are reasons for believing that some molecules are electrically unsymmetrical even in the absence of the applied field. If the centers of gravity of positive and negative electricity do not coincide in the molecule, the molecule will act electrically like an electric doublet or dipole and will possess a permanent electric moment μ. These

* Data from C. T. Zahn, *Physik. Z.*, **33**, 730 (1932), and from the books of Debye and Smyth.

dipoles will tend to have random orientations in the absence of the applied electric field, but as the field is applied the dipoles will turn and will tend to orient themselves in the direction of the field; this turning motion constitutes an additional current in the dielectric and so increases the dielectric constant and consequently the molal polarization. But the thermal motion of the molecules operates to produce a random distribution of the molecules and to hinder the orientation of the molecules in the direction of the applied electric field, and as the temperature is raised, the orientation of the molecules is more and more hindered until finally at infinite temperature, we may assume that no orientation of the molecular dipoles in the field is possible and the molal polarization P will then fall to the value given by the Clausius and Mosotti Eq. (12). According to the classical statistics of Maxwell and Boltzmann (the Maxwell and Boltzmann distribution law will be considered in detail in connection with the Debye and Hückel theory of activity coefficients) the number of molecules in the volume element dV, whose dipole axes make an angle θ with the direction of the field is proportional to

$$e^{-\frac{U}{kT}}dV, \tag{13}$$

where U is the energy of the molecule in the location under consideration, k is Boltzmann's constant, and T the absolute temperature ($\frac{3}{2}kT$ is the kinetic energy of the molecule, $\frac{1}{2}kT$ for each degree of freedom).* The energy is given by the equation

$$U = \boldsymbol{\mu}\mathbf{F}. \tag{14}$$

Since each molecule has a component of moment, $\boldsymbol{\mu} \cos \theta$, in the direction of $\mathbf{F}$, the average moment $\overline{\mathbf{m}}$ in the direction of $\mathbf{F}$ is given by the expression

$$\overline{\mathbf{m}} = \frac{\int_0^\pi e^{\frac{-\mu\mathbf{F}}{kT}} \boldsymbol{\mu} \cos \theta dV}{\int_0^\pi e^{\frac{-\mu\mathbf{F}}{kT}} dV}. \tag{15}$$

If we introduce the abbreviation

$$\frac{\boldsymbol{\mu}\mathbf{F}}{kT} = x,$$

*See I. Estermann, *Erg. d. Exakten Naturwissensch.*, **8**, 262 (1929).

the solution of Eq. (15) is

$$\overline{\mathbf{m}} = \left(\operatorname{ctnh} x - \frac{1}{x}\right)\boldsymbol{\mu}. \tag{16}$$

Equation (16) may be simplified to

$$\overline{\mathbf{m}} = \frac{1}{3}x\boldsymbol{\mu}$$

or

$$\overline{\mathbf{m}} = \frac{1}{3}\frac{\mu^2\mathbf{F}}{kT}, \tag{17}$$

since x is very small in the actual cases under consideration. By adding to the temporary moment $\mathbf{m}$ the average moment due to the permanent electrical asymmetry of the molecule, $\overline{\mathbf{m}}$, we obtain, instead of Eq. (9), the equation

$$\mathbf{I} = n(\mathbf{m} + \mathbf{m}) = n\mathbf{F}\left(\alpha_0 + \frac{1}{3}\frac{\mu^2}{kT}\right). \tag{18}$$

Going through the derivation analogous to the derivation used in obtaining Eq. (11), we obtain instead of Eq. (11)

$$\frac{D-1}{D+2} = \frac{4\pi n}{3}\left(\alpha_0 + \frac{1}{3}\frac{\mu^2}{kT}\right) \tag{19}$$

and instead of Eq. (12),

$$\frac{D-1}{D+2}\frac{M}{d} = \frac{4\pi}{3}\mathbf{N}\left(\alpha_0 + \frac{1}{3}\frac{\mu^2}{kT}\right) \equiv P \tag{20}$$

or

$$P = A + \frac{B}{T}, \tag{21}$$

where A and B are constants. Equation (21) is called Debye's equation.*

The Debye equation is derived on the assumption that every molecule possessing a permanent electric moment is free to move when the electric field is applied and that each molecule has a random orientation in the absence of the field. There must not be any intermolecular attractions or molecular association which would cause the dipoles to be partially oriented in the absence of

* P. Debye, *Physik. Z.*, **13**, 97 (1912).

the field. Furthermore, the viscosity of the medium must be low enough for the molecules to orient themselves and the frequency of the applied alternating current must not be so great that the orientation of the molecules does not follow the fluctuations in the current.

In applying and testing the Debye equation, it is customary to plot the polarization P against the reciprocal of the absolute temperature $1/T$. Such a plot for the hydrogen halides is given in Fig. 4. If the Debye equation is applicable, the results should follow along a straight line having a slope equal to the constant B

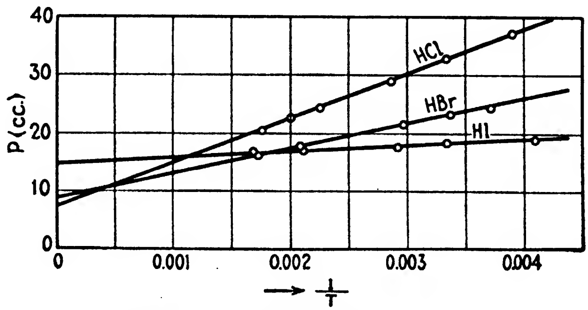


Fig. 4.—Test of the Debye equation.

of Eq. (21) and having an intercept on the P axis at $1/T$ equals zero (when the temperature is infinite) equal to A. All the results agree very well with the Debye predictions and verify the essential correctness of the theoretical equation.

It will be noticed that hydrogen chloride has the steepest slope and the smallest intercept of the three gases. This means that hydrogen chloride has the largest permanent electric moment since the slope of the line for hydrogen chloride is the greatest. The slope of the line and the electric moment are connected by the equation [from Eqs. (20) and (21) after introduction of the numerical values of **N** and k]

$$\mu = 0.0127 \times 10^{-18}\sqrt{B}. \tag{22}$$

From Eq. (22) it is apparent that the permanent electric moment is proportional to the square root of the slope of the line, the greater the electric moment, the greater the slope. Substances that have no permanent electric moment show no change of the

polarization with change of temperature so that the slope of curves plotted as in Fig. 4 would be equal to zero.

Although hydrogen chloride has the largest electric moment, its polarizability α_0 is the smallest, as can be judged from the intercept on the y-axis from which the polarizability can be calculated. This means that for the three molecules considered, the hydrogen chloride molecule is the least elastic and the hydrogen iodide molecule is the most elastic. There are more electrons in the hydrogen iodide molecule, and as the external field is applied, these electrons are more easily distorted from their symmetrical positions than are the electrons in the hydrogen chloride molecules.

The order of magnitude of the electric moment is 1×10^{-18} c.g.s. e.s.u., and this is to be expected from the definition of the electric moment, which is charge times length, since the unit charge is 4×10^{-10} e.s.u. and the distance between atoms is of the order of magnitude of 1×10^{-8} cm.; e.s.c.g.s. units $\times 10^{+18}$ are called debyes.

Electric Moments in Relation to the Structure of Inorganic Molecules.—We shall now consider the actual values of the electric moment for a number of inorganic molecules, seeing in what respect the electric moments confirm our previous ideas as to atomic and molecular structure, in what respect the data enable us to decide between two possible structural formulas, and in what respect the data enable us to predict the structural formulas of compounds about which we have no other information.

The simplest chemical substance whose electric moment has been determined is undoubtedly argon. Argon is a monatomic gas whose atoms are built up of a positive nucleus surrounded by 18 electrons. From the great chemical inertness of argon we believe that the electrons are symmetrically arranged about the nucleus; this belief is substantiated by the fact that the atomic spectrum of argon shows that the electrons are all in "closed" shells about the nucleus and that the resultant of the angular momenta of the electrons is equal to zero. Hence, when considering the atom from a distance, we can treat the electrons as if all the electrons of the atom were located in the nucleus. This being the case, argon should not have a permanent electric moment because the effective positions of the positive and

negative charges in the atom coincide. Experimentally, argon has a zero moment as can be seen from Table II, which includes the electric moments of some inorganic substances as taken from the book of Smyth.

TABLE II.—ELECTRIC MOMENTS OF SOME INORGANIC MOLECULES IN DEBYE UNITS

Formula	μ	Formula	μ	Formula	μ
A	0	CS_2	0	H_2O	1.85
H_2	0	CO_2	0	H_2S	0.95
N_2	0	SnI_4	0	NH_3	1.49
O_2	0	CO	0.11	$SbCl_3$	3.6
Cl_2	probably 0	HCl	1.03	SbI_3	0.4
Br_2	0	HBr	0.78	$AgClO_4$	4.7
I_2	0	HI	0.38	SO_2	1.61

In the case of argon, the datum for the electric moment merely confirms ideas that were previously held concerning its atomic structure. In the case of symmetrical diatomic molecules such as H_2, N_2, O_2, Cl_2, Br_2, and I_2 we should also expect the electric moments to be zero, and such is indeed the case. Carbon monoxide is interesting because of the similarity between it and the nitrogen molecule. Langmuir* in 1919 pointed out the great similarity between the physical properties of these two gases and postulated that the electronic structure of the carbon monoxide and nitrogen molecules must be nearly identical. The neutral carbon atom has 6 extranuclear electrons, the oxygen atom has 8 extranuclear electrons, and the molecule which results from the combination of carbon and oxygen has 14 electrons. The nitrogen molecule also contains 14 extranuclear electrons. Lewis† states, however, "if we are to assume precisely the same electron structure for N_2 and for CO, the latter must be electrically polarized in the sense that the oxygen is positive and the carbon negative, since in the neutral state the oxygen atom has one more electron than the nitrogen atom, while the carbon has one less. Such polarization would probably suffice to explain

* I. LANGMUIR, *J. Am. Chem. Soc.*, **41**, 904 (1919).

† G. N. LEWIS, "Valence and the Structure of Atoms and Molecules," p. 127, Chemical Catalog Company, Inc., New York, 1923.

the difference in chemical behavior. On the other hand, if the electrons in carbon monoxide are shifted in such manner as to diminish the degree of polarization of the molecule, the distortion of valence shells so produced might equally well account for the chemical reactivity of carbon monoxide." In a study of the electronic structure of diatomic molecules as evidenced by band-spectra data, Mulliken* concludes that the electrons in a molecule are not to be arbitrarily assigned to either of the atoms which constitute the molecule, but that at least the valence electrons of both atoms must be considered as belonging to the molecule as a whole. The experimental value for the electric moment of carbon monoxide, 0.1×10^{-18}, gives a clue to the electronic structure of carbon monoxide. The electric moment is nearly zero, which indicates that in the formation of carbon monoxide the electrons undoubtedly shift in such a way as to bring about a nearly symmetrical electrical arrangement so that the centers of gravity of the positive and negative electricity lie close together. It is easy to calculate the electric moment that the carbon monoxide molecule should have if all the electrons retain the same position in the molecule that they hold in the separate atoms, with the exception of the extra electron on the oxygen atom. If this extra electron goes over completely to the carbon so that there are 7 electrons about the carbon nucleus and 7 electrons about the oxygen nucleus, the carbon atom will become a negative ion and the oxygen atom will become a positive ion. From the moment of inertia of the carbon monoxide molecule, which is obtained by a study of the infrared absorption bands, it is possible to calculate that the distance between the carbon and oxygen nuclei is 1.14×10^{-8} cm. If, according to our picture above, the net positive charge of the oxygen atom and the net negative charge of the carbon atom are located at the two nuclei, respectively, the electric moment of the carbon monoxide should be equal to the unit charge times the distance or

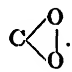
$$\mu = qr = (4.77 \times 10^{-10})(1.14 \times 10^{-8})$$
$$\mu = 5.44 \times 10^{-18} \text{ e.s.u.}$$

The measured value is 0.11×10^{-18}; hence we can conclude that our simple picture of the carbon monoxide molecule outlined

* R. S. Mulliken, *Chem. Rev.*, 9, 347 (1931).

above is incorrect and that the electrons in the carbon monoxide molecules are so arranged that the centers of gravity of the positive and negative electricity lie very close to each other.

By means of electric-moment measurements we are able to decide between two possible structures of the carbon dioxide molecule, *viz.*, the symmetrical structure, O=C=O, or the triangular structure,



The band-spectra data seem to favor the linear model. This conclusion is borne out by the value for the electric moment which is zero. The similarity between sulfur and oxygen would lead one to expect that the electric moment of carbon disulfide would be zero if the moment for carbon dioxide is zero; this prediction is verified experimentally.

Turning now to some electrically unsymmetrical molecules, we find that all of the hydrogen halides have appreciable electric moments. If we assume that in the formation of hydrogen chloride, the electron from the hydrogen goes over to the chlorine completely so that the chlorine ion has the same symmetrical electronic structure that argon has, the electric moment of the molecule should be equal to the elementary charge times the distance between the hydrogen and chlorine nuclei or 6.06 debyes. The experimental value is much smaller, 1.03 debyes, therefore we must conclude that the electrons about the chlorine do not have the symmetrical inert gas arrangement, but that they are distorted owing to the force of the electric field about the hydrogen ion. In other words, the positive hydrogen ion causes the electrons about the chlorine nucleus to move in its direction so that the center of gravity of the negative electricity does not coincide with the chlorine nucleus but must lie somewhere between the hydrogen and chlorine nuclei. Connecting up this conclusion with our previous discussions as to degree of ionization, dissociation, etc., of substances in solution, we can say that the hydrogen chloride molecule is not completely ionized in the gaseous condition. As the hydrogen chloride dissolves in water, it dissociates into its two ions and the ionization of each molecule on dissociation becomes complete.

Two decidedly polar molecules are the water and ammonia molecules. The structural formula for water commonly used by chemists is H—O—H, but this form of the water molecule would have a zero electric moment if both of the hydrogen ions were equidistant from the oxygen ion. The only electrically unsymmetrical linear model for the water molecule is a model in which

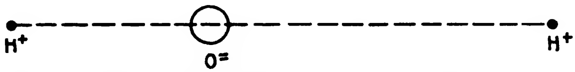


FIG. 5.—Unsymmetrical linear model of the water molecule.

one hydrogen ion is farther away from the oxygen ion than is the other, as represented in Fig. 5. Heisenberg and Hund* have shown that any linear model of the water molecule that is electrically unsymmetrical is also at the same time unstable to lateral and tangential displacements of the hydrogen ion; hence a linear water molecule having a permanent electric moment is incapable of existing. The ammonia model in which the three hydrogen ions and the nitrogen ion are in the same plane, but unsymmetrically arranged, is also unstable. However, if the hydrogen ions in water are attached to the oxygen ion in a triangular arrangement with an acute angle between the lines joining the centers of the hydrogen ions with the center of the oxygen ion as pictured in Fig. 6, a stable, electrically unsymmetrical model is obtained. Theoretical calculations also indicate that the only possible electrically unsymmetrical model for ammonia is a pyramid with the three hydrogen ions forming the triangular base and the nitrogen ion the apex of the pyramid. Chemical substances similar to water and ammonia† such as hydrogen sulfide, phosphine, and arsine, all of which have appreciable electric moments, may be expected to have triangular or pyramidal structures. Wierl‡ has recently determined the molecular structure of a single molecule of some gases by the

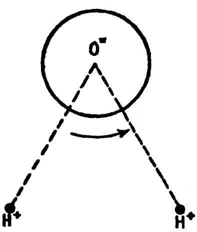


FIG. 6.—A possible triangular model for the water molecule which is electrically unsymmetrical.

* See P. DEBYE, *op. cit.*, Chap. IV.

† C. P. Smyth and C. S. Hitchcock, *J. Am. Chem. Soc.*, **56**, 1084 (1934), have recently measured the dielectric constants of solid ammonia, hydrogen sulfide, and methyl alcohol.

‡ R. WIERL, *Ann. Physik*, **8**, 521 (1931); *C. A.*, **25**, 2886 (1931).

method of electron diffraction and finds, in agreement with the conclusions of the electric moment study, that carbon dioxide and carbon disulfide have a linear molecular form.

Electric Moments in Relation to the Structure of Organic Molecules.—Dielectric-constant measurements have been applied most extensively to the study of the structure of organic molecules, and on the whole it can be said that the results confirm in a high degree the pictorial models of organic compounds commonly used by the organic chemist.* Let us consider first aliphatic compounds.

The simplest organic compound is methane which at a very early date in the history of organic chemistry was given the well-known structure

$$\begin{array}{c} H \\ | \\ H—C—H. \\ | \\ H \end{array}$$

The electric moment of this compound is zero as is to be expected from its symmetrical structure. Similarly the electric moment of carbon tetrachloride is also zero. Carbon tetrachloride has been shown by Wierl to have a tetrahedral structure as in Fig. 7. It is probable that methane also has this symmetrical tetrahedral structure. The substitution of less than 4 chlorine atoms in the methane molecule gives rise to electrical asymmetry and the compounds $CHCl_3$, CH_2Cl_2, and CH_3Cl have appreciable electric moments, as indicated by the data collected in Table III. (The appendix to Vol. 30, *Trans. Faraday* Soc., lists values of μ for over 1,000 different compounds.)

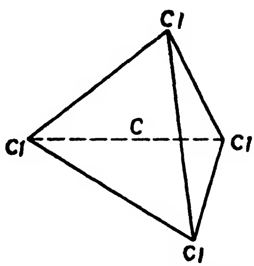


FIG. 7.—Tetrahedral model of carbon tetrachloride.

The most unsymmetrical molecule is methyl chloride; further substitution of chlorine reduces the electric moment. The electric moment of methyl chloride is considerably larger than

* C. P. Smyth and J. W. Williams have each reviewed this subject matter in *Chem. Rev.*, **6**, 549, 589. See also H. Sack, *Erg. d. Exakten Naturwissensch.*, **8**, 307 (1929).

the moment of hydrogen chloride (1.03 debye); this may be due in part to the fact that the methyl group cannot penetrate into the chloride ion in the way that the hydrogen ion penetrates.

TABLE III.—ELECTRIC MOMENTS OF SOME ALIPHATIC ORGANIC MOLECULES IN DEBYE UNITS

Formula	μ	Formula	μ
CH_4	0	CH_3OH	1.68
CCl_4	0	C_2H_5OH	1.70
CH_3Cl	1.86	CH_3OCH_3	1.29
CH_2Cl_2	1.51	$C_2H_5OC_2H_5$	1.12
$CHCl_3$	1.05	CH_3CHO	2.7?
C_2H_5Cl	2.02	C_3H_7CHO	2.46
n-C_3H_7Cl	2.04	CH_3COCH_3	2.80
n-C_4H_9Cl	1.97	CH_3COOH	1.4?
iso-C_4H_9Cl	1.96	CH_3COOCH_3	1.7
sec-C_4H_9Cl	2.09	$CH_2{=}CH_2$	0
ter-C_4H_9Cl	2.15	$CH_3CH_2CH{=}CH_2$	0.37

The methyl group is undoubtedly distorted by the chloride ion, and it is reasonable to assume that additional moments or displacements of charges are induced in the methyl group and the chlorine structure so that the electric moment of methyl chloride is greater than that of hydrogen chloride. It is interesting to note the effect of increasing the length of the carbon chain. At first, in ethyl chloride, the electric moment rises, due to induction of additional moments in the added CH_2 group, but further additions of CH_2 groups do not change the electric moment, propyl and butyl chlorides having about the same electric moments as ethyl chloride. There is a slight difference between the iso-, secondary, and tertiary butyl chlorides, probably because of additional moments induced in the CH_3 groups by the chlorine.

The electric moments of the alcohols and ethers are interesting because of the similarity of these substances to water. Methyl alcohol may be thought of as water in which one of the hydrogens has been replaced by a methyl group. The substitution of the methyl group for the hydrogen lowers the electric moment, possibly because the methyl group causes a widening of the angle between the axes of the two doublets formed between the oxygen and the methyl and the oxygen and the hydrogen. If both the

hydrogens are replaced by methyl groups to form methyl ether, the electric moment is lowered to 1.29 debyes, the ordinary chemical formula indicates that methyl ether is symmetrical, but the existence of an electric moment proves that the molecule must be distorted into a triangular shape similar to water. The lower electric moment of methyl ether as compared with water or methyl alcohol indicates that the angle between the axes of the two doublets between the methyl groups and oxygen is widened due to a repulsion of one methyl group for the other. In ethyl ether the electric moment is still lower as might be expected.

The aldehydes and ketones have very high electric moments, including even paraldehyde whose ordinary ring structure looks symmetrical. The moment must be largely, if not entirely, due to the carbonyl group, C=O, since both the aldehydes and the ketones have large electric moments. This is interesting when it is remembered that carbon monoxide, CO, has an almost negligible electric moment. The aldehydes and ketones may be considered as Y-shaped structures with the oxygen at the base of the Y, the carbon at the branching of the forks and the other two groups at the tip of the two forks. The angle between the forks is not particularly important in determining the electric moment of the molecule. The acids include both the carbonyl group and the hydroxyl group in their molecules, the resulting combination being called, of course, the carboxyl group. Apparently, the carboxyl group has a distinctly lower electric moment than the carbonyl group. The electric moment of the hydroxyl group must be oriented in a direction to oppose the electric moment of the carbonyl group.

Ethylene has no electric moment, which proves that double bonds are not polar. However, the presence of a double bond in a compound like ethyl-ethylene causes a slight electrical asymmetry so that a small electric moment results.

The electric moments of aromatic compounds are interesting. Benzene has no electric moment; hence it is possible to measure at low concentrations the electric moments of substances dissolved in benzene. Williams* and his coworkers have also shown that the electric moments of a number of substances are

* J. W. Williams and E. F. Ogg, *J. Am. Chem. Soc.*, **50**, 94 (1928); Williams and Schwingel, *ibid.*, **50**, 362 (1928).

the same in the three different solvents, benzene, carbon disulfide, and hexane. For example, they found the following values for the electric moment of nitrobenzene dissolved in the above-mentioned solvents, 3.90, 3.89, and 3.89 debyes, respectively. (See below, however.)

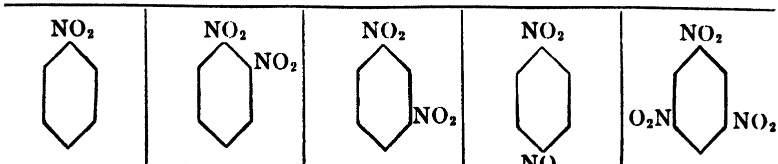
In general we may say that the monosubstituents of benzene lack electrical symmetry and that all have electric moments. The magnitude of the electric moment depends upon the group substituted, CH_3 gives the smallest effect, COOH, Cl, and OH follow in the order named, while NO_2 gives the largest effect. The electric moments of these molecules are tabulated with other data in Table IV.

Table IV.—Electric Moments of Some Aromatic Organic Molecules in Debye Units

Formula	μ	Formula	μ
C_6H_6	0	p-$C_6H_4(NO_2)_2$	0
$C_6H_5CH_3$	0.4	1.3.5 $C_6H_3(NO_2)_3$	0
C_6H_5COOH	0.8?	o-$CH_3C_6H_4NO_2$	3.75
C_6H_5Cl	1.52	m-$CH_3C_6H_4NO_2$	4.20
C_6H_5OH	1.70	p-$CH_3C_6H_4NO_2$	4.50
$C_6H_5NO_2$	3.9	o-$ClC_6H_4NO_2$	4.0
o-$C_6H_4(NO_2)_2$	6.0	m-$ClC_6H_4NO_2$	3.3
m-$C_6H_4(NO_2)_2$	3.7	p-$ClC_6H_4NO_2$	2.45

The electric moments of the disubstituted benzenes depend upon the location of the substituted groups. In this respect it is interesting to compare the electric moments of the dinitrobenzenes with their structures as represented in Table V. Ortho-

Table V.—Electric Moments in Debye Units and Structural Formulas of the Nitrobenzenes

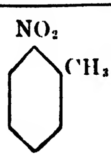
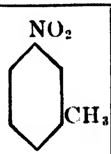
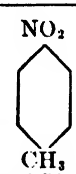
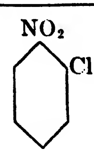
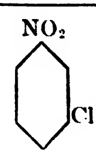


μ = 3.9	6.0	3.7	0	0

dinitrobenzene has an electric moment almost twice that of nitrobenzene, but substitution of the second nitro group in the meta position decreases the moment considerably, while substitution in the para position forms a symmetrical molecule with zero electric moment. The symmetrical trinitrobenzene also has a zero electric moment. Evidently the substitution of the groups results in the formation of small electric doublets which reinforce each other in the *o*-dinitrobenzene, or cancel each other partially as in the *m*-dinitrobenzene, or completely as in the *p*-dinitrobenzene and in the trinitrobenzene.

If the two substituted groups in the benzene ring are not identical, the moments of the two groups may reinforce each other or partially cancel each other depending upon their electrical character and upon their relative positions in the ring. The nitro and chloride groups are undoubtedly negative in character and the methyl group is undoubtedly positive; in methyl chloride, for example, it is entirely reasonable to suppose that the methyl group carries an excess of positive electricity and the chlorine atom an excess of negative electricity. If these groups are substituted in the benzene ring, we should expect that a positive group would enhance the electric moment of the molecule if substituted para to a negative group or would reduce the electric moment if substituted para to a positive group. Similarly a negative group substituted ortho to a negative group would increase the electric moment, but if substituted para to a negative group, the electric moment should be decreased. It is possible to test these ideas and at the same time to confirm our notions as to the electrical nature of the groups by studying the data and the structures of the nitrotoluenes and the chloronitrobenzenes as given in Table VI.

TABLE VI.—ELECTRIC MOMENTS IN DEBYE UNITS AND STRUCTURAL FORMULAS OF THE MONONITROTOLUENES AND THE CHLORONITROBENZENES

					
μ = 3.75	4.20	4.50	4.0	3.3	2.45

The results are entirely in accord with our expectations and agree with the common structural representations of these compounds. At this point it might be stated that the study of electric moments indicates that the plane hexagonal model of benzene corresponding to the Kekulé formula is still the most plausible model of this much discussed substance.

Group Rotation and the Theoretical Calculation of Electric Moments.—Up to this point we have been content to discuss the significance of the electric moments in a rather qualitative fashion without making any attempt to analyze the data quantitatively. Considerable information can be obtained concerning the details of the structure of organic compounds if we make attempts to calculate theoretically their electric moments. In so doing we assign to each characteristic organic group a value for its electric moment. The value of the moment for a group in any particular compound must be considered a vector quantity because the resultant electric moment of the molecule as a whole will depend upon the direction of orientation of the dipoles within the molecules (provided there are more than one present in the molecule). Not only must we consider the magnitude and direction of the separate moments in the molecule, but we must also consider any interactions that may occur between the dipoles, and we must also consider a possible rotation of the groups within the molecule. Thus, it is seen that the situation is rather complex, but in the case of certain compounds very accurate theoretical calculations of the molecular moments have been carried out. Eucken and Meyer, Wolf, Højendahl, Williams, Eyring, Smyth, Zahn, Smallwood and Herzfeld, Gross, and others have made valuable contributions in this field.*

As an example let us consider the theoretical calculation of the electric moment of *p*-xylylene dichloride, $CH_2ClC_6H_4CH_2Cl$ (Fig. 8*a*), as carried out by De Bruyne, Davis, and Gross. In this compound we have two CH_2Cl groups attached to the benzene ring in the para position to each other. Each CH_2Cl

* See H. Sack, *Erg. d. Exakten Naturwissensch.*, **8**, 307 (1929), for an extensive bibliography. C. T. Zahn, *Phys. Rev.*, **38**, 521 (1931); **40**, 291 (1932); *Physik. Z.*, **33**, 400, 686, 730 (1932); **34**, 570 (1933); Henry Eyring, *Phys. Rev.*, **39**, 746 (1932); Smallwood and Herzfeld, *J. Am. Chem. Soc.*, **52**, 1919 (1930); Smyth and Walls, *ibid.*, **54**, 2261 (1932); J. M. A. de Bruyne, Rose M. Davis, and Paul M. Gross, *ibid.*, **55**, 3936 (1933).

induces moments in the phenyl group, but as these induced moments are inversely proportional to the cube of the distance, it is assumed that the CH_2Cl groups will have no effect upon each other. On the basis of symmetry it might be expected that *p*-xylylenedichloride would have a zero electric moment unless the C—Cl moment is oriented at an angle to the axis of the phenyl group, see Fig. 8*b*. If the C—Cl moments were parallel to the axis of the benzene ring, angle θ equal to zero, and if both moments were directed toward the ring, the resulting moment would be zero. It is necessary, therefore, to determine the angle θ that the C—Cl moment makes with the axis of the benzene ring before we can calculate the resulting moment of the compound. This is

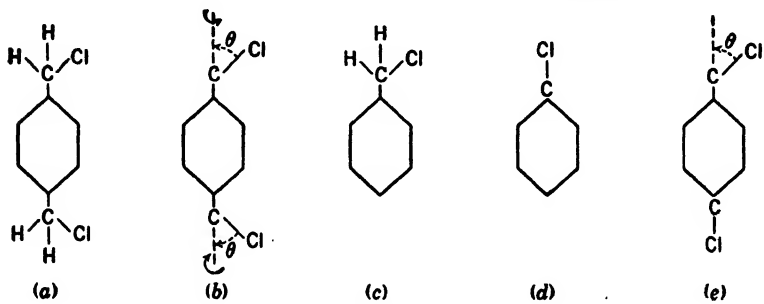


FIG. 8.

done by De Bruyne, Davis, and Gross in the following way: The observed moment of benzyl chloride is 1.85 (all moments will be given in debyes) and may be considered as being practically independent of the direction of the vector representing the bond moment, Fig. 8*c*. The observed moment of chlorobenzene is 1.56 and as seen in Fig. 8*d*, the direction of the vector representing the electric moment is probably directed along the axis of the ring. The compound *p*-chlorobenzyl chloride contains both the chlorobenzyl electric moment and the moment due to the chlorine-carbon bond of the chlorobenzene, Fig. 8*e*. The electric moment of this molecule will be equal to the resultant of the electric moments due to the substituted groups and by measuring the electric moment we can then calculate the angle θ for the angle between the axis of the benzene ring and the vector representing the electric moment of the CH_2Cl group. It will be remembered that the resultant moment of the molecule as a whole

is the vector sum of the separate moments. Since the magnitude of these vector quantities is known, 1.85 and 1.56, the angle between them can be calculated if we know their vector sum. By measuring the electric moment of *p*-chlorobenzyl chloride, Fig. 8*e*, we can find the vector sum of the moments due to the two substituted groups. In this way we can calculate the angle θ of Fig. 8*b*. The electric moment of *p*-chlorobenzyl chloride is 1.70 and from this value angle θ is calculated to be 59° 5′. This calculation assumes that the two substituted groups are so far apart that there are no interactions between them. Knowing the angle θ it is now possible to calculate the electric moment of *p*-xylylene dichloride (Fig. 8*a*), from the equation

$$\mu_{\text{calcd.}} = \mu_i\sqrt{2}\sin\theta, \tag{23}$$

where μ_i is the electric moment of a single CH_2Cl group as substituted in the benzene ring

$$\mu_i = \mu_{C_6H_5CH_2Cl} = 1.85.$$

An understanding of the physical significance of Eq. (23) may be gained if it is remembered that it is the molal polarization P that we measure and that the molal polarization is a linear function of the square of the electric moment in Eq. (20). To get the average resultant electric moment for *p*-xylylene dichloride we must take the average of the squares of the electric moments that the molecule has as the CH_2Cl groups rotate about the axis of the benzene ring as indicated in Fig. 8*b*. If the two CH_2Cl groups are *trans* to each other, the resultant moment is zero; if the two CH_2Cl groups are *cis* to each other, the moment of the molecule is $2\mu_i \sin\theta$. If we assume that all rotational positions are equally probable, the calculated moment becomes

$$\mu_{\text{calcd.}} = \sqrt{\frac{(2\mu_i \sin\theta)^2 + 0^2}{2}}$$

or Eq. (23).*

Calculating the electric moment of *p*-xylylene dichloride from Eq. (23) we get 2.26, whereas the observed value is 2.23 debyes. This agreement is very good and indicates in all probability

* This derivation does not pretend to be rigid. See Williams, *Z. physik. Chem.*, **138**, 75 (1928), for the first derivation of Eq. (23).

that the two CH_2Cl groups are rotating freely about the axis of the benzene ring. In case the substituted groups are ortho or meta to each other, the calculated values do not agree so well with the observed values. This is due, probably, to interactions between the two substituted groups inasmuch as in these compounds the groups are presumably nearer together.

Zahn* has investigated 1, 2-dichloroethane and finds that the electric moment of this compound increases with rise of temperature. Calculating the electric moment of this compound assuming free rotation about the C—C bond axis and no interaction between the groups, Zahn obtains the value 2.54. The value of the electric moment for each C—Cl bond is 1.8 and since the vectors representing the separate moments are parallel to each other whether in the *cis* or *trans* position (as can be readily seen if one builds a tetrahedral model of dichloroethane in space) provided no distortion of the molecule occurs, the resultant electric moment is equal to $1.8\sqrt{2}$ [from Eq. (23)] or 2.54. This value is only approximate because the two C—Cl bonds are so close to each other that there is undoubtedly some interaction between the two. Actually Zahn finds that the measured values for the electric moment of dichloroethane vary from 1.12 at 31°C. to 1.54 at 270°C. If the groups could rotate freely about the C—C bond axis, the electric moment would be independent of temperature. The small value of the moment and its variation with temperature are explained by Zahn on the assumption of restricted rotation. Perhaps the two chlorine atoms repel each other to such an extent that only very infrequently does the molecule assume the *cis* form. Zahn believes that the two C—Cl bonds do not rotate on the average more than 40° from the *trans* position. This assumption accounts for the low value of the observed electric moment and also accounts for the increase of the electric moment with increase of temperature, because with increase of temperature one would expect that the two groups could get closer and closer to the *cis* position due to the increased energy of rotation.

There is another effect that change of temperature seems to have on the electric moment if measurements of μ are made in

* C. T. Zahn, *Phys. Rev.*, **38**, 521 (1931); **40**, 291 (1932); See also, A. E. Stearn and C. P. Smyth, *J. Am. Chem. Soc.*, **56**, 1667 (1934).

solution. It was stated previously that the electric moment of a substance when in solution was independent of the nature of the solvent. This is not quite true apparently since careful measurements of the electric moment, or rather of ${}_\infty P_2$, the polarization of the solution due to a mole of solute at infinite dilution, indicate a small change of the permanent electric moment with change of solvent. Some data obtained by Müller* for C_6H_5Cl in a number of solvents at 20°C. are given in Table VII.

TABLE VII.—MOLAL POLARIZATION OF C_6H_5Cl AT INFINITE DILUTION IN A NUMBER OF SOLVENTS. 20°C.

Solvent	C_6H_{14}	C_6H_{12}	$C_{10}H_{18}$	CCl_4	C_6H_6	C_2Cl_4	CS_2
D of solvent...	1.91	2.02	2.16	2.23	2.28	2.30	2.64
${}_\infty P_2$..........	86	84	83	81	81	79	75.5

The molal polarization due to the chlorobenzene definitely decreases with increase of dielectric constant. This change of μ with change of the dielectric constant has also been established for a number of other substances; if μ is zero, however, there is no effect, the molal polarization of ClC_6H_4Cl, for example, being independent of the nature of the solvent. Now if μ increases with decrease of the dielectric constant, we should also expect μ to increase with increase of temperature due to the same causes since the dielectric constant decreases with increase of temperature. If we consider substances for which free or restricted rotation has no bearing on the polarization such as methylene chloride (CH_2Cl_2), it is discovered that the product of P_0T where P_0 is that part of the polarization due to dipole orientation is not a constant as it should be according to the Debye theory, but increases with increasing temperature (decreasing dielectric constant).† There is no theory at present which accounts for this influence of the solvent on the electric moment.

In this discussion of electric moments we have restricted ourselves to a consideration of the polarization due to orientation

* F. H. MÜLLER, *Trans. Faraday Soc.*, **30**, 729 (1934); see also *Physik. Z.*, **33**, 732 (1932); H. O. JENKINS, *Nature*, Jan. 20, 1934; *Trans. Faraday Soc.*, **30**, 739 (1934).

† F. H. MÜLLER, *Physik. Z.*, **35**, 346 (1934); See also H. O. JENKINS, *Trans. Faraday Soc.*, **30**, 739 (1934); *J. Chem. Soc.*, **1934**, 480.

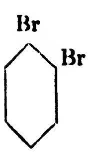
and to the so-called "optical" or electronic polarization, the polarization due to the shift of electrons within the molecule. If the atoms of a molecule are displaced relatively to each other in the electric field, a polarization is produced which is called the atomic polarization. At the present time, values of the atomic polarization are very uncertain; hence the subject of atomic polarization has been omitted from this chapter. For a recent critique of atomic polarization the reader is referred to a paper by Sugden.*

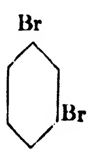
Exercises

1. Plot the following values for the molal polarization of ethyl acetate as a function of $1/T$, where T is the absolute temperature. Calculate the electric moment of ethyl acetate. Does the electric moment vary with temperature?

t, °C.	$P_{cc.}$
29.1	88.0
53.5	83.2
76.2	79.5
106.4	75.0
193.5	65.6

2. Predict qualitatively the electric moment of the following compounds; give reasons.


(a)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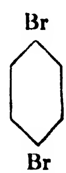
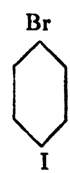

(c)


(d)


(e)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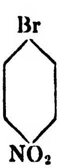
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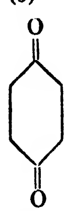
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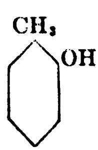
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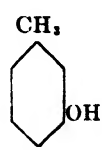
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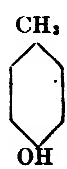
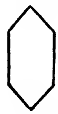

(k)

* S. Sugden, *Trans. Faraday Soc.*, **30**, 734 (1934).

(*l*) C_2Cl_6, (*m*) CH_2I_2, (*n*) CH_2ICH_2I, (*o*) dibenzyl,

OCH_3



OCH_3.

(*p*)

3. Predict the electric moment of $CH_2ClCH_2CH_2Cl$.
4. Prove that the angle θ of Fig. 8*b* is equal to 59°42′.

CHAPTER XIII

MOLECULAR RAYS

A molecular ray or beam is composed of a number of neutral atoms or molecules all moving in the same direction so that there are no collisions between the gas particles in the beam. It is obvious that if all the molecules are streaming in the same direction (and with the same speed), no molecule will suffer a collision until the bounding walls of the apparatus are encountered. A considerable body of information may be obtained by studying the motion of these molecular rays both in field free space and in magnetic and electric fields.

From experiments on molecules in inhomogeneous electric fields it is possible to determine electric moments; it is for this reason that we shall consider molecular rays at this point.*

Production of Rays.—At ordinary temperatures and pressures the motion of gas molecules is random, the molecules suffer countless collisions per second, and as a consequence their motion undergoes rapid changes in direction. A ray of molecules, nearly collisionless and unidirectional, may be obtained by heating the molecules to a rapid motion in an oven and then allowing them to stream through a slit system into a chamber where the mean free path of the molecule is large in comparison with the dimensions of the chamber. An apparatus for the production of molecular rays is shown schematically in Fig. 1. This apparatus which is the type used by Estermann,† consists, first, of an oven A in which is placed the substance whose molecules are to constitute the molecular beam. The oven is heated electrically by means of resistances around the phosphor bronze block at B. The temperature of the oven can be measured by a thermocouple, and the oven should be so constructed that the temperature of

* For a detailed discussion of molecular rays see R. G. J. Fraser, "Molecular Rays," The Macmillan Company, New York, 1931, and W. H. Rodebush, *Rev. Mod. Phys.*, **3**, 392 (1931).

† Estermann, *Z. physik. Chem.*, **1 B**, 161 (1928).

the slit S_1 is the maximum temperature of the oven. This is to prevent material from condensing in the slit and thus clogging it up.

An important part of the apparatus is the slit system, S_1, S_2, which makes possible the formation of the molecular ray. Inside the oven A the molecules are roaming about in chaotic motion, but a certain number of them move in the direction of the slit S_1 and effuse through it toward S_2. A certain fraction of the molecules

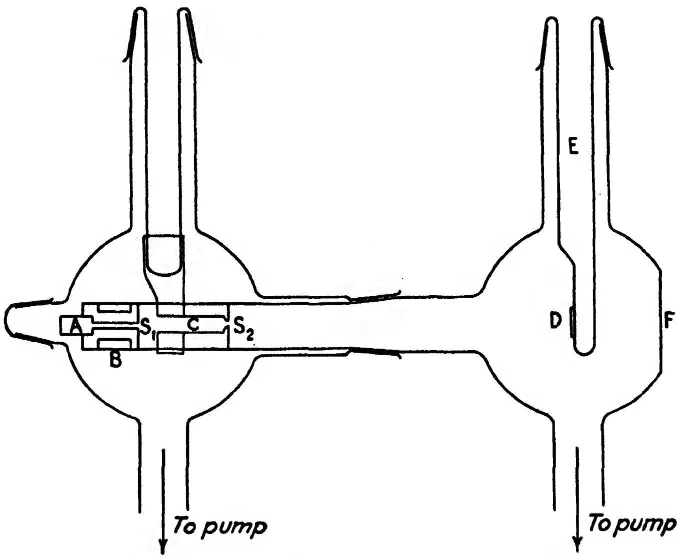


FIG. 1.—Schematic diagram of molecular-ray apparatus.

effusing through S_1 will never get to S_2 but will collide with the walls of the collimator chamber C. Since it is undesirable that these "alien" molecules remain in the collimator chamber, the sides of C are kept cool so that the molecules which collide with it are condensed. The slit S_2 is called the image slit, for it is the shape of this slit that determines the shape of the image of the beam on the target D.

A certain fraction of the molecules which effuse through S_1 fly directly toward S_2 and effuse through S_2. It is the molecules that finally get through the slit S_2 that constitute the molecular ray. The gas pressure in the detection chamber is kept very low so that

the molecules are able to move from the slit S_2 to the target D without colliding with any other molecule.

The molecular ray will not retain the exact dimensions of the slit S_2 but will tend to spread out into an umbra and penumbra. This is made clear by reference to Fig. 2. Region A on the target is the dense image of the slit, while the regions B and B are the partially shaded regions, the penumbra.

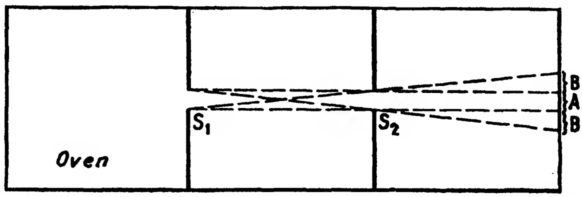


FIG. 2.—Schematic diagram of a molecular ray showing umbra and penumbra on target.

Deflection of Rays.—Although the molecules (or atoms) that make up the molecular ray are electrically neutral, the molecular ray may be deflected by either an electric or a magnetic field under certain conditions. Let us assume that the proper magnetic or electric apparatus is inserted into the detection chamber between the slit S_2 and the target D. The beam or perhaps part of the beam will be deflected or distorted from its true course, and the magnitude of the deflection can be measured on the target.

Let us consider first the deflection of molecules in a magnetic field. There are two general cases in which no deflection will occur. Provided the molecules are neutral, and the definition of a molecular ray requires that the molecules be neutral, the ray will not be deflected if it passes through a homogeneous magnetic field. A homogeneous magnetic field is one in which the field strength, H, is everywhere the same or, mathematically speaking,

$$\frac{dH}{dx} = 0,$$

where x represents distance. A homogeneous magnetic field is produced between two plane pole pieces of a magnet as in Fig. 3. The molecular ray will also not be deflected if the molecules and atoms making up the ray have no net resultant magnetic moment. The magnetic moment is the magnetic analog of the electric moment (see Chap. XII) and is defined by the equation

$$\mu = ml, \tag{1}$$

where μ is the magnetic moment, m is the strength of the two poles of the magnet, and l is the distance between the poles. If a little magnet of moment μ be placed between the pole pieces of the magnet represented in Fig. 3, the magnet will orient itself in the field, but it will not be displaced toward either pole. Similarly, an electric dipole of moment μ placed in a homogeneous electric field will orient itself in the field, but it will suffer no net displacement in either direction.

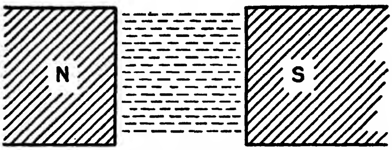


FIG. 3.—Magnet for the production of a homogeneous magnetic field.

The situation is quite different, however, if the molecular ray travels through an *inhomogeneous* magnetic field. Each molecule in the beam will now be acted on by a force

$$f = \mu\frac{\partial H}{\partial x} \cos \theta, \tag{2}$$

where f is the force, μ is the magnetic moment, θ is the constant angle between the vector $\boldsymbol{\mu}$ and the lines of force, and dH/dx (x = distance) is the inhomogeneity of the field. The force f will impart to the molecule of mass m an acceleration (in the direction of the field) of f/m; the net deflection x of the beam is therefore (when μ is oriented parallel to the field)

$$x = \frac{1}{2}\frac{f}{m}\frac{l^2}{\bar{v}^2}, \tag{3}$$

where l is the length of path *in the field* and $\bar{v}$ is the velocity of the molecules. Equation (3) tells us that the deflection of the ray which takes place in the field is proportional to the square of the distance the molecules travel in the field and to the first power of the force acting on the molecule. The total deflection at the target will be greater than the deflection suffered by the rays between the pole pieces. Rodebush* gives as the total deflection at the target,

$$x = \frac{1}{2}\frac{f}{m\bar{v}^2}(l^2 + 2ll_1), \tag{4}$$

* W. H. RODEBUSH, *Rev. Mod. Phys.*, **3**, 399 (1931).

where l_1 is the distance the beam travels after leaving the pole pieces.

In order to obtain a magnetic field with an inhomogeneity of 10^4 gauss per centimeter; a magnet called by Fraser* the Hamburg set-up (because it was invented by Stern and Gerlach working in Hamburg) has been used. One pole piece of the magnet consists in a wedge (Fig. 4), while the other pole piece has a deep narrow channel cut in it opposite the wedge. The strength of the magnetic field varies considerably with distance with this arrangement; hence a large value for the inhomogeneity is obtained. The Hamburg set-up has the additional advantage of a constant value of dH/dx immediately before the entrance of the channel. This means that the force acting on the molecular ray is everywhere the same. In Fig. 4 the molecular ray is shown by the heavy line; its direction of motion is perpendicular to the plane of the paper.

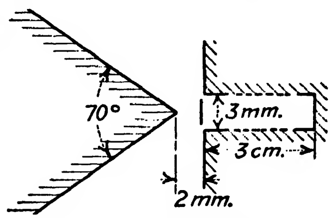


FIG. 4.—The Stern-Gerlach magnet for the production of a magnetic field of uniform inhomogeneity.

In treating of magnetic deflections of molecular rays we are limited entirely to the deflection of atoms since the deflection of molecules has not yet been studied. In the case of the electric deflection of molecular rays, however, we must deal with molecules and not atoms, and because of this the treatment becomes more complicated. Atoms may have a resultant magnetic moment, but they have no permanent electric moment. Molecules may have permanent electric moments (see Chap. XII).

It is possible to obtain electric fields of very high inhomogeneity, and one might expect that it would be possible to deflect electrically the molecular rays to a much greater extent than is possible magnetically. This is not in general the case, however, due to the temperature rotation of the molecules which acts to reduce the effective electric moment of the molecule. Fraser† has shown that for a diatomic molecule with two degrees of free-

* FRASER, *op. cit.*, p. 120.

† FRASER, *op. cit.*, p. 160. See also ESTERMANN and FRASER, *J. Chem. Phys.*, **1**, 390 (1933).

dom (pure rotator) the time-averaged moment $\bar{\mu}$ in terms of the permanent electric moment μ is approximately

$$\bar{\mu} = \mu \cdot \frac{\mu X}{4kT}, \tag{5}$$

where X is the electric field strength, k is Boltzmann's constant, and T is the absolute temperature. If the field strength is 150,000 v. per centimeter, Fraser calculates that at room temperature

$$\bar{\mu} \sim 3 \times 10^{-3}\mu.$$

The deflections in the electric deviation experiments on diatomic

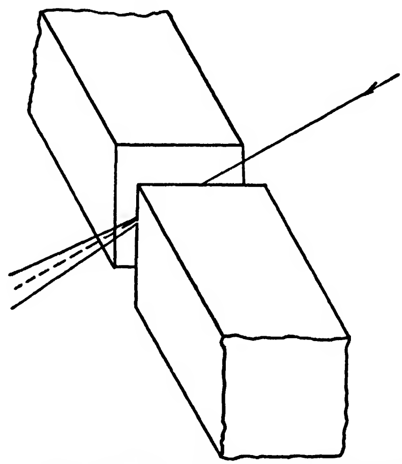


FIG. 5.—Pole pieces for production of the Rabi field.

molecules will be, therefore, of the same order of magnitude as the magnetic deviation of the atomic beams.

The inhomogeneous electric field is best produced by a condenser of the Rabi type. Rabi's* arrangement, which is illustrated in Fig. 5, may also be used for the production of inhomogeneous magnetic fields. It has the advantage that the total change of the field strength over the path of the beam may be calculated, even if the inhomogeneity at any particular point is unknown. The molecular beam which passes at an angle between the pole pieces (see Fig. 5) is made to traverse the

* RABI, *Z. Physik*, **54**, 190 (1929).

inhomogeneous zone completely. In the Rabi-type condenser the inhomogeneity exists at the outside edges of the pole pieces. The pole pieces are flat and are parallel to each other. When the apparatus is used for the production of an inhomogeneous electric field, sparking at the sharp edges may be avoided by rounding the edges off.

Detection of Rays.—Before discussing the actual results of the deflection experiments, we shall describe several of the different methods used to detect the molecular ray as it strikes the target. The detection of the ray is one of the chief experimental difficulties in the study of molecular rays, and the accuracy of the investigations depends largely on the sensitivity of the method used in detecting the ray. Since the atoms or molecules making up the ray are electrically neutral, neither a photographic plate nor the usual form of ionization chamber may be used as the detector. Instead, investigators of molecular rays are forced to use condensation targets, chemical targets, or special types of ionization chambers. Other methods have been used, but they will not be described here.* A condensation target is illustrated in Fig. 1. It consists of a glass or metal plate *D* kept cool by liquid air in the vessel *E*. For some substances it is unnecessary to use liquid air in *E*; it is only necessary to keep the target cool enough so that the molecules which strike it will condense on the target and accumulate as a permanent deposit. If the molecules do condense on the target (some molecules having a very low boiling point like hydrogen would not condense on the target at the temperature of liquid air), it is only necessary to allow the molecular ray to stream through the apparatus until a deposit has collected which is dense enough to be seen. The deposit may be viewed or photographed through a window *F*, provided a totally reflecting prism is inserted into the detector chamber at the proper point. Molecular rays composed of the following substances have been detected by means of the condensation target: most of the metals, some alkali halides, water, nitric anhydride (N_2O_5), and several organic compounds. In certain cases it is possible to intensify the deposit or to render visible an

* See R. G. J. Fraser, "Molecular Rays," pp. 24 *ff.*, The Macmillan Company, New York, 1931, for a detailed discussion of different detecting devices.

invisible trace by developing the deposit either by allowing silver to precipitate from the solution upon the target or by allowing a metallic vapor to condense upon it. The possibility of developing the image is due to the tendency of additional atoms to condense on particles already condensed.

Chemical targets in which the impinging molecules react chemically with the substance composing the target are strictly limited in their applicability. Molecular rays of atomic hydrogen on striking the target reduce pale yellow MoO_3 to blue MoO_2 which can be seen against the pale yellow MoO_3 background. Molecular rays of atomic oxygen on striking a target composed of litharge oxidize the pale yellow PbO to brown PbO_2. These targets are quite sensitive to atomic oxygen and hydrogen, but they have not been used for many other types of molecular rays.

The chemical target and the condensation target are additive detectors in the sense that the effect of the molecular ray on the target accumulates until the traces become visible. Nonadditive detectors are devices such as monometers which measure the pressure set up by the molecular ray when it falls upon a narrow slit, hot wire gauges which utilize the change of resistance suffered by a hot wire when it is cooled by a gas at low pressure, thermopiles, bolometers, radiometers, and finally surface-ionization detectors. These devices measure the instantaneous effect that the molecular ray has upon their properties. Let us consider the surface-ionization detector.*

In the description of Gurney's quantum mechanical theory of electrochemistry (Chap. XXIX) it will be pointed out that a metal having a low work function (work necessary to remove an electron from a metal) will give up an electron to a metal having a high work function. Cesium has a much greater tendency to give off electrons than has tungsten; hence a cesium atom coming in contact with a tungsten wire will remain on the surface of the tungsten wire as a positive ion because of its low ionization potential. Now Langmuir and Kingdon† discovered that the cesium *ions* will evaporate from tungsten if the tungsten is heated above 1200°K. Potassium and rubidium behave similarly, and sodium and lithium will also do the same if the tungsten

* Taylor, *Z. Physik*, **57**, 242, (1929).

† Langmuir and Kingdon, *Proc. Roy. Soc.*, A **107**, 73 (1925).

wire is oxygenated by heating in an oxygen atmosphere (0.1 to 0.01 mm. pressure of oxygen) at 1500°K. The evaporation of positive ions from the tungsten wire constitutes a current of electricity which can be measured by means of a galvanometer. In the case of molecular rays composed of any of the alkali metals the rays are allowed to fall upon the hot tungsten wire. The atoms striking the wire evaporate as positive ions and migrate through the gas phase to a cylinder which surrounds the wire and which is kept at a negative potential. The deflections of the galvanometer measure the strength of the current due to the positive ions, and thus they are a measure of the intensity of the molecular ray.

Estermann and Stern* have recently developed a very sensitive and quite general method for the quantitative estimation of the intensity of a molecular ray. They allow the molecular ray to stream into a chamber in which a negative space charge has been built up by heating a tungsten filament placed therein. The walls of the chamber constitute the anode, between the walls and the filament a small accelerating potential is applied (about 20 v.). The field is large enough so that the electrons are accelerated to a velocity which is sufficient to cause ionization of the neutral molecules of the beam streaming into the chamber, but low enough so that an adequate space charge is built up around the filament. The positive ions produced neutralize the space charge, thus enabling the filament-anode current to increase. A measurement of the filament-anode current can in this way yield accurate information concerning the intensity of the molecular ray.

Results Obtained by the Molecular-ray Experiments Using Inhomogeneous Magnetic Fields.—Perhaps the most important experiment carried out in the field of molecular rays was the Stern and Gerlach† experiment. This experiment permitted a direct test of the quantum theory to be made. The change in energy ΔU, due to placing a magnetic doublet of moment μ in a magnetic field H, is

$$\Delta U = \mu_i H. \tag{6}$$

According to the classical theory, values of ΔU vary continuously

* Estermann and Stern, *Z. Physik*, **85**, 135 (1933).

† Gerlach and Stern, *Ann. Physik*, **74**, 673 (1924).

from zero to ΔU, but the quantum theory tells us that energy is not perfectly continuous but is really composed of finite amounts called quanta. Applying these two theories to Eq. (6) it becomes clear that the classical theory allows any value of μ_i from zero to $\mu \cos (\mu H)$, while the quantum theory allows certain discrete values of μ_i which are defined by the relation

$$\mu_i = gM\mu_B. \tag{7}$$

M is the magnetic quantum number which may be predicted for any given energy state of the atom from spectroscopic theory, g is the Landé factor so-called, and μ_B is the quantum unit of the magnetic moment (the "Bohr magneton")

$$\mu_B = \frac{\epsilon h}{4\pi m_0 c} = 0.918 \times 10^{-20} \text{ erg gauss}^{-1}. \tag{8}$$

In Eq. (8), h is Planck's constant, ϵ and m_0 are the charge and mass of the electron, and c is the velocity of light. The Landé factor g is calculated (in certain cases) from the equation

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \tag{9}$$

The J, S, and L values are obtained from a study of atomic spectra. To illustrate the use of these equations let us consider silver, which was the substance originally investigated by Gerlach and Stern. Silver in its normal energy state (molecular-ray experiments are performed on atoms in their normal states) has a single s electron outside its closed orbits. The resultant magnetic moment of all closed orbits is zero; hence we need to consider the magnetic moment due to the single electron only. The magnetic quantum number of the electron M_s is $\pm\frac{1}{2}$. Since we do not have to consider the magnetic moment due to the orientation of the orbits in space L, the resultant of the M_l's is zero. Therefore, in the case of silver in its normal state, the value of S is $\pm\frac{1}{2}$ and the value of J, the resultant of L and S is also $\pm\frac{1}{2}$ since L is zero. This method of obtaining L, S, and J is known as the Russell-Saunders (LS) coupling and is not valid for all the atoms. The positive and negative signs of S and J mean that the vectors representing these numbers are to be taken first in one direction and then in the opposite direction.

In Eq. (9) J, S, and L are always positive. Substituting the value of $\frac{1}{2}$ for S and J into Eq. (9), we obtain a value of g equal to 2 and a value of gM equal to ± 1, since M equals $\pm\frac{1}{2}$. The physical significance of the plus and minus sign is that the electron spin is oriented in one direction or in the opposite direction. Thus, from the quantum theory, we see that μ_i can take on only the values $\pm\mu_B$ [from Eq. (7)].

Suppose now that a beam of silver atoms passes through the inhomogeneous field of a Hamburg set-up. The theoretical deflection that is predicted on the basis of the classical theory consists of a broadening of the beam with a maximum of intensity at the location of the undeflected beam. The quantum theory predicts, however, that the ray will be separated into two distinct branches with a minimum of intensity at the location of the undeflected beam. The separation into the two branches is due to the two possible values of gM, *i.e.*, ± 1.

Actually the experimental findings agree exactly with the prediction that gM can be only plus one or minus one. The molecular ray was deflected into two branches with a minimum of intensity at the location of the undeflected beam. This experiment of Stern and Gerlach constitutes a brilliant verification of the quantum theory.

The alkali metals, copper, gold, and hydrogen all give results similar to silver. Zinc, cadmium, and mercury molecular rays show no deflection, which means that the magnetic moments of the atoms are zero. Tin and lead atoms likewise have no magnetic moment. The case of thallium is interesting. Here the normal state of the atom gives L equal to 1, hence g has the value $\frac{2}{3}$ and $\frac{4}{3}$, and $\pm M$ is either $\frac{1}{2}$ or $\frac{3}{2}$. Under these conditions one might expect the molecular ray composed of thallium atoms to split into six components,

M	g	gM
$+\frac{1}{2}$	$\frac{2}{3}$	$+\frac{1}{3}$
$-\frac{1}{2}$	$\frac{2}{3}$	$-\frac{1}{3}$
$+\frac{1}{2}$	$\frac{4}{3}$	$+\frac{2}{3}$
$-\frac{1}{2}$	$\frac{4}{3}$	$-\frac{2}{3}$
$+\frac{3}{2}$	$\frac{4}{3}$	$+2$
$-\frac{3}{2}$	$\frac{4}{3}$	-2

Actually the value of g equal to $4/3$ is due to a metastable state which is present to a negligible extent in the beam. Hence we find gM equal only to $\pm 1/3$. Experiments by Leu* confirmed these values of gM.

TABLE I.—VALUES OF gM OBTAINED BY THE STERN-GERLACH EXPERIMENT AFTER RODEBUSH*

Element	$\pm gM$
Sn, Pb, Cd, Pd	0
Tl	$1/3$
Bi	0.85 ± 0.015
H, Li, Na, K, Ag, Cu, Au	1
S_2, Ni	2?
O	0, $3/2$, 3
Sb, Fe	?

* W. H. RODEBUSH, *Rev. Mod. Phys.*, **3**, 410 (1931).

Rodebush has collected the results obtained by the Stern-Gerlach experiment. His table is repeated here (Table I). These gM values confirm the values theoretically calculated from spectroscopic data.

Of particular interest to chemists are the molecular-ray experiments which led to a knowledge of the extent of dissociation of molecules. As an example of the application of molecular rays in this field we may describe the recent experiment of Lewis† on sodium vapor. Lewis measured the deflection of the sodium rays with the surface-ionization detector which permits a relative accuracy of 0.01 per cent to be obtained. His results are illustrated in Fig. 6, where the left-hand curve A is a plot of the galvanometer deflections in the absence of the inhomogeneous magnetic field. There is a single maximum in intensity, no branches, and the width of the curve demonstrates the width of the ray at the detector. The right-hand curve is the intensity plot with field applied, the two branches being due to the deflection of the magnetic atoms while the small central maximum, curve B, is produced by the presence in the beam of nonmagnetic molecules, Na_2.

The ratio between the intensity of the undeflected portion of the molecular ray and the intensity of the ray before the

* LEU, *Z. Physik*, **41**, 551 (1927).

† L. C. LEWIS, *Z. Physik*, **69**, 786 (1931); see also FRASER, "Molecular Rays," p. 189, The Macmillan Company, New York, 1931, and RODEBUSH, *op. cit.*, p. 409.

magnetic field is applied does not give the ratio between the molecules in the oven and the atoms in the oven for three reasons:

1. The molecular ray in the absence of the magnetic field contains both atoms and molecules.

2. Since the atoms are one-half as heavy as the molecules, they will stream out of the oven more frequently in the ratio of $\sqrt{2}:1$.

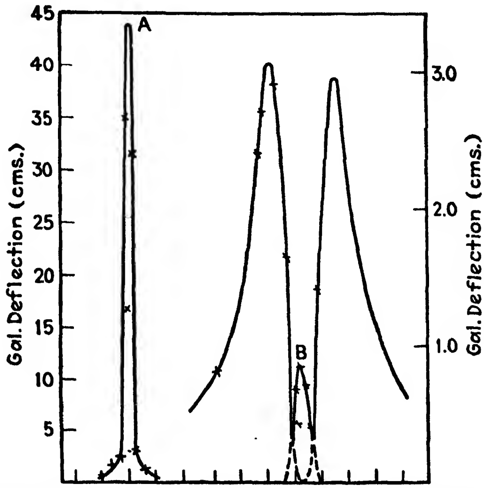


FIG. 6.—The deflection of a mixed beam of sodium atoms and molecules in an inhomogeneous magnetic field.

3. The ionization chamber counts each molecule as two atoms since the tungsten wire is hot enough to dissociate the sodium molecule. If x is the ratio between the maxima of curves B and A (see Fig. 6), *i.e.*,

$$x = \frac{I_B}{I_A} \tag{10}$$

and if ϵ is the ratio between the partial pressure of the molecules and atoms in the oven, *i.e.*,

$$\epsilon = \frac{P_m}{P_a}, \tag{11}$$

then Lewis shows that

$$\epsilon = \frac{x}{1 - x}\frac{\sqrt{2}}{2}. \tag{12}$$

The dissociation constant, at constant pressure, of the reaction

$$Na_2 \rightleftarrows 2Na, \tag{13}$$

is

$$K_p = \frac{P^2_{Na}}{P_{Na_2}} = \frac{P_{Na}}{\epsilon} = \frac{P}{\epsilon(1+\epsilon)}, \tag{14}$$

where P is the total pressure in the oven. Equations (14), (12), and (10) enable K_p to be calculated from the molecular-ray experiments. Lewis's results for sodium are given in Table II. He also determined the dissociation constant for potassium and lithium.

TABLE II.—DISSOCIATION OF SODIUM VAPOR AS OBTAINED BY THE MOLECULAR-RAY METHOD

T	x	P	$\log K_p$
630	0.0165	0.104	0.936
655	0.0180	0.220	1.223
672	0.0214	0.357	1.356
684.5	0.0234	0.495	1.459
719	0.0304	1.18	1.744

The heat-content increase for the reaction of dissociation calculated by means of Eq. (16), Chap. XX, is +16,800 cal. per mole. Thus, by the molecular-ray method it is possible to determine the dissociation constant of gases, and from the temperature coefficient of log K, the heat of dissociation may be obtained.

Molecular rays also offer the possibility of measuring nuclear magnetic moments; it is beyond the scope of this book, however, to consider nuclear moments.*

Results of the Deflection of Molecular Rays by Inhomogeneous Electric Fields.—When a molecular ray composed of monatomic molecules is subjected to the deflecting force of an inhomogeneous

* See I. I. RABI, J. M. B. KELLOGG and J. R. ZACHARIASEN, *Phys. Rev.*, **46**, 157, 163 (1934); RABI and COHEN, *ibid.*, **46**, 707, 713 (1934). In order to obtain a measurement of nuclear magnetic moments it is necessary to deflect the molecular beam in an inhomogeneous magnetic field of fairly low intensity, around 350 gauss per centimeter, where there is strong coupling between the nuclear and electronic spins. In the usual Stern-Gerlach experiment the inhomogeneity of the field is much larger, 10^4 gauss per centimeter, so that the nuclear and electronic spins are completely decoupled. Otherwise a more complicated splitting of the ray would occur.

magnetic field, only those molecules are deflected which possess magnetic moments in the absence of the applied field, but this is not the case when a ray composed of diatomic molecules is subjected to an inhomogeneous electric field. All the molecules in the ray are deflected by the inhomogeneous electric field whether the molecules are polar or nonpolar, nevertheless it is possible to gain some information concerning the electrical nature of the molecule inasmuch as a ray composed entirely of nonpolar molecules is merely deflected by the inhomogeneous electric field while a ray composed of polar molecules is both deflected and broadened. The deflection of the nonpolar molecules is due to the fact that the applied field polarizes the molecule and induces in the molecule a temporary electric moment which is always in the direction of the field. Since the induced electric moments of every molecule are always in the direction of the field and presumably equal to each other, each molecule will be deflected by the inhomogeneous field in the same direction and to the same extent (provided, of course, that they all have the same velocity); hence the ray will be deflected as a whole and will not be changed in width. On the other hand, if the molecules are polar, they will possess electric moments in the absence of the field; these permanent electric moments will persist in the presence of the field and since the molecules are rotating due to their thermal energy, the electric moments will not all be in the direction of the field at every moment. Because of this, different molecules will be deflected to a different extent and the ray will be broadened as well as deflected. Estermann's* data given in

TABLE III.—RESULTS OF THE ELECTRIC DEFLECTION OF MOLECULAR RAYS

Substance	μ, debye units	Width of ray, mm.
Diphenyl	0	0.15
Diphenyl methane	< 0.4	0.15
Diphenyl ether	1.0	about 0.30
Benzophenone	2.5	about 0.60
o-$C_6H_4(NH_2)COOCH_3$	1.0	about 0.25
m-$C_6H_4(NH_2)COOCH_3$	2.4	about 0.5
p-$C_6H_4(NH_2)COOCH_3$	3.3	about 0.7

* ESTERMANN, *Erg. d. Exakten Naturwissensch.*, **8**, 285 (1929)

Table III illustrate the extent to which the molecular rays are broadened as a function of the permanent electric moment of the compound. Temporary electric moments are also induced in polar molecules so that the molecular rays composed of polar molecules also suffer deflections due to this effect.

The calculation of the electric moment from molecular-ray experiments is very complicated, and the results are not yet as accurate* as desired. This method of measuring the electric moment has the advantage of being applicable in cases where other methods are not applicable, *e.g.*, in the case of pentaerythritol, $C(CH_2OH)_4$, which is insoluble in nonpolar solvents and which cannot be vaporized to a sufficiently high pressure without decomposition. The molecular-ray method is interesting in that it gives evidence, independent of dielectric-constant measurements, for the existence of permanent electric moments. It is also possible that molecular-ray experiments will be of importance in studying the variation of μ with temperature since in the molecular-ray work it is possible to measure μ without varying the temperature; *i.e.*, at a single temperature.

Exercises

1. Derive Eq. (3).

2. Predict the type of spectrum that would be obtained on deflecting magnetically an atomic beam of cesium.

3. The ground state of oxygen is represented by the symbol $^3P_2$ (triplet P sub 2) which means that L is 1, J is 0, 1, or 2, and S is 1 (the multiplicity of the state is 3, and S is therefore 1 since the multiplicity is equal to $2S + 1$). Calculate all possible values of gM and compare the result with the data of Table I. It should be noted that M is the resultant of J in the magnetic field and can have all integral values from 0 to $\pm J$. Remember that for each value of J there is but one value of g.

* See I. Estermann and R. G. J. Fraser, *J. Chem. Phys.*, **1**, 390 (1933). H. Scheffers, *Physik., Z.*, **35**, 425 (1934), however, seems to have brought the molecular-ray method to an accuracy approaching that of the dielectric-constant method.

CHAPTER XIV

THE MEASUREMENT OF ELECTRICAL POTENTIAL DIFFERENCE

Introduction.—The widespread occurrence of electrical potential throughout the universe indicates that its existence is fundamental for action, that it accompanies practically all phenomena, and that if the potential becomes everywhere the same so that equilibrium exists, the world would become lifeless; for, has not Donnan remarked "equilibrium is death"? Electrical potential difference may arise in a number of ways. A chemical reaction can produce a difference of potential as can also the dilution of a salt solution if these two phenomena occur in a galvanic cell. Potentials may exist across membranes that are permeable to some ions and not to others, and they may exist between two immiscible phases in contact, although it will never be possible to measure the magnitude of phase boundary potentials unequivocally. Potentials may arise during the motion of material bodies through a liquid medium or during the motion of the medium through a material body. Finally, we can mention the existence of electrical potentials in living organisms and cells, electrical potentials whose origin is still obscure. Because of the universality of electrical potentials, it is important in electrochemistry to study methods of measuring them and to consider theories which have been advanced to explain the observed results.

The Voltmeter.—The simplest and least accurate method of measuring the voltage consists in using the voltmeter. The voltmeter is similar to an ammeter, but instead of having a shunt for the current, it has a high internal resistance so that only a small current will flow through the instrument. The commercial voltmeters are convenient for rapid estimations of the potential difference between two terminals of a cell or two points along a conductor, but they give erroneous values if the resistance of the unknown circuit is high. All the IR drop should be in the

voltmeter, but this is not true when the unknown cell has a high internal resistance.

Potentiometers of the Poggendorf Type.—For the accurate measurement of the electromotive force (the electrical potential difference developed by the conversion of chemical into electrical energy) it is necessary to use Poggendorf's* method. Poggendorf's apparatus is shown diagrammatically in Fig. 1.

The fundamental principle of this type of potentiometer is that a potential difference along *ab* is balanced against an unknown electromotive force (e.m.f.) X so that no current flows in the circuit *XGca*. In order to obtain a convenient source of potential

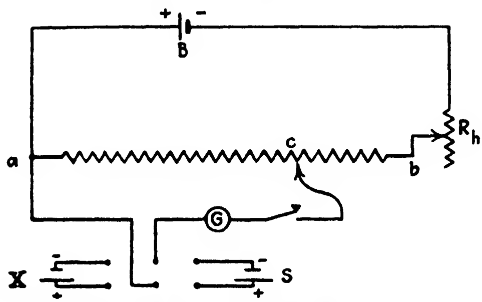


FIG. 1.—Schematic diagram of the Poggendorf potentiometer.

difference, p.d., a battery B causes a current to flow through the resistance slide wire *acb*. The potential fall along *ab* is given by Ohm's law, $E = IR$; hence it is evident that if the current remains constant, the p.d. is directly proportional to the resistance. The current through *ab* depends upon the voltage of the working battery B and upon the total resistance of the circuit, *acbB* which is equal to the resistance of *ab*, R_{ab}, plus the internal resistance of the battery R_B plus the resistance of the rheostat R_h. If the resistances R_B and R_{ab} remain constant (which is a reasonable assumption), the current through *ab* will depend upon the e.m.f. of the working battery. This e.m.f. generally falls as the battery is used; hence it is necessary to decrease the total resistance of the circuit in order to keep the current through *ab* constant. This is accomplished by decreasing the resistance of the rheostat R_h. In practice it is necessary to adjust the current

* See F. T. Gucker, Jr., and F. van Atta, *J. Chem. Ed.*, **8**, 1157 (1931), for a description of an excellent lecture-table-demonstration potentiometer.

through *ab* to its correct value every few minutes; the method of doing this will be described shortly.

Assuming that the current through *ab* is constant, it is possible to adjust the movable contact *c* along *ab* so that any p.d. between *a* and *c* from zero (when *c* coincides with *a*) to a value slightly below the e.m.f. of the working cell (when *c* coincides with *b*) may be obtained. This p.d. is then balanced against any other p.d. or e.m.f. until the two are equal. When the p.d. along *ac* is equal to the unknown e.m.f. of X, for example, no current will flow through the indicating device G. If the p.d. along *ac* is slightly greater than the unknown e.m.f., positive current will flow through the indicating device to the right (as illustrated in Fig. 1) causing the indicating device to deflect in one direction. If the p.d. along *ac* is slightly less than the unknown e.m.f., positive current will flow through the indicating device to the left, causing it to deflect in the opposite direction. If the p.d. exactly balances the e.m.f., the indicating device will not deflect at all; hence it is possible to measure the unknown e.m.f. of X in terms of the p.d. along *ac*. Before considering how we may standardize the p.d. along *ac* to a known value, let us consider what effect, if any, the internal resistance of the unknown cell X and the resistance of the electrical leads of the circuit *acGX* will have upon the measured p.d. As current flows through X, the true e.m.f. of X will be reduced by the amount I_xR_x, or

$$E_x - I_xR_x = \text{p.d.}$$

But at balance no current at all flows through the circuit *acGX*; hence I_xR_x is zero and the measured p.d. turns out to be independent of the internal resistance of the cell and equal to the true e.m.f. of the unknown cell. This is very fortunate since some unknown cells to be described later on in this book have internal resistances of the order of magnitude of a hundred million ohms. It can be similarly proved that the resistances of the leads have no effect.

Having found a value of the p.d. along *ab* which is equal to the e.m.f. of X, it is now necessary to convert this value into volts in order to know the e.m.f. of X in volts. For this purpose we can replace X by a cell, S, whose e.m.f. we know. The sliding contact *c* is next set along *ab* at a point which corresponds in figures

to the known e.m.f. of S. Then the current through ab is increased or decreased by means of the rheostat R_h until the p.d. from a to c is equal to the known e.m.f. S. When the current through ab has in this way been correctly adjusted, the readings along the slide wire ab actually represent standard volts. (Actually the slide wire is standardized before the e.m.f. of the unknown cell is measured.)

Indicating Devices.—The indicating device G may be a galvanometer, an electrometer, or a vacuum-tube system. The moving-coil galvanometer, sometimes called the D'Arsonval galvanometer, is illustrated in Fig. 2.

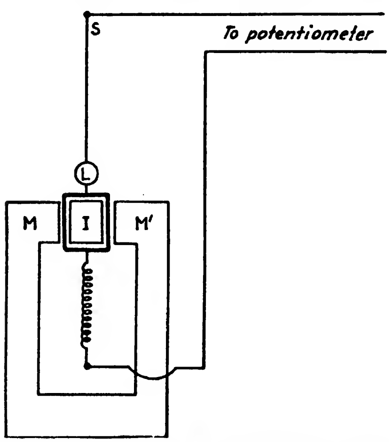


FIG. 2.—The moving-coil galvanometer.

The moving coil through which the current flows is suspended by a fine wire S which serves as a lead to the moving coil. The bottom part of the coil is made steady by a loosely coiled metallic spring which also serves as a lead. The coil hangs between the north and south pole of the permanent magnet M and M', and inside it is a stationary soft iron core I. The lines of magnetic force run horizontally across the air gap, while the current in the moving coil flows perpendicularly to the lines of magnetic force. The turning moment on the coil due to the current cutting the magnetic lines of force is in a direction perpendicular to both the current and the magnetic field, *i.e.*, perpendicular to the plane of the diagram. Hence as a current flows through the coil, it will turn until the restoring moment due to the twist in the spring is just equal to the deflecting moment due to the current. The motion of the coil is observed and magnified by means of a beam of light which is reflected from the mirror on the suspension L to a distant screen or ground glass plate. The direction of the deflection of the light depends upon the direction of current flowing through the coil. Reversal of the current reverses the deflection. In this way the galvanometer can indicate whether

or not the p.d. of the slide wire *ab* (Fig. 1) is greater than, less than, or just equal to, the e.m.f. of the unknown cell. The deflection of the galvanometer is proportional to the magnetic field and to the current flowing through the moving coil. Galvanometers such as the Leeds and Northrup type *R* have permanent magnets at *M* so that the magnetic field is constant; however, care should be taken that the moving system does not collect dirt or dust as accumulated matter might change its period.

The galvanometer must be critically damped; that is, the galvanometer terminals must be short-circuited by a resistance of the proper magnitude. If the galvanometer terminals are not short-circuited, the galvanometer will swing back and forth without ever seeming to come to rest. If the galvanometer is "overdamped," or in other words if the resistance of the shunt is too low, the moving coil will not swing back and forth but will approach its correct position very slowly. If the galvanometer is correctly damped, the moving coil will swing to its correct position in the minimum of time and will not swing too far either in deflecting or in returning to its zero position. The optimum damping resistance of a galvanometer depends upon the particular galvanometer used; the correct value is generally given by the manufacturer. The physical principle of damping is due to a current induced in the moving coil by the coil cutting the magnetic lines of force; this current, according to Lenz's law, is induced in such a direction as to oppose the motion by which it is induced. Hence the swinging coil causes the induction of currents in its own circuit which bring it to rest. It is important in using the galvanometer not to allow an excessive current to flow through the instrument. This might cause the suspension to break. Most potentiometers are so constructed that in making a measurement the current flowing through the galvanometer first passes through a series resistance of 100,000 ohms. This enables the operator to obtain an approximately correct setting of the potentiometer without the danger of ruining the galvanometer. When the p.d. of the potentiometer and the e.m.f. of the unknown cell are nearly balanced, the current flowing through the galvanometer is small; hence under these conditions the entire p.d. is measured by the galvanometer without introduction of the 100,000 ohms series resistance.

When the total resistance of the unknown cell is comparatively small, such as 100 ohms, a small difference of potential such as 0.0001 v. between the p.d. of the slide wire and the e.m.f. of the unknown cell can cause sufficient current to flow through the galvanometer to produce a deflection. However, if the resistance of the unknown cell is a million ohms, the current through the circuit due to 0.0001 v. is only 0.0001/1,000,000 or 1×10^{-10} amp., and this is too small to turn the coil of an ordinary galvanometer. However, the Leeds and Northrup high-sensitivity galvanometer (their number 2290) gives a light deflection of 1 mm. at 1 meter distance when a current of 1×10^{-11} amp. flows through the coil. If the resistance of the unknown cell is over ten million ohms, even this galvanometer is too insensitive.

A possible method, independently invented by Brown, by Jones and Kaplan, by Beans and Oakes, and by Morton, for the e.m.f. measurement of a cell with a very high internal resistance,* is to allow the small current which flows through the cell when the e.m.f. and the p.d. are nearly balanced to charge up a condenser slowly. When the charge on the condenser has been built up to a value high enough to actuate a ballistic galvanometer, the condenser is discharged by tapping a key, and it is possible to observe the deflection of the galvanometer. If the e.m.f. of the cell is exactly in balance with the p.d. of the potentiometer, no current will flow to the condenser, and the galvanometer will show no deflection when the charge on the condenser is discharged through it. The galvanometer must be a ballistic galvanometer; that is, its period must be so long that the moving coil will not begin to swing in the time it takes for the condenser to discharge. This method of determining the null point (the point at which the e.m.f. and the p.d. are exactly in balance) is reliable, but the time necessary for the condenser to become sufficiently charged makes the procedure rather tedious. Some data obtained by the author† in measuring the e.m.f. of a glass electrode cell (see Chap. XXV) having an internal resistance of approximately 20 megohms (meg = million) are given in Table I.

* W. E. L. Brown, *J. Sci. Instruments*, **2**, 12 (1924); Grinnell Jones and B. B. Kaplan, *J. Am. Chem. Soc.*, **50**, 1853 (1928); H. T. Beans and E. T. Oakes, *ibid.*, **42**, 2116 (1920); C. Morton, *J. Sci. Instruments*, **7**, 187–190 (1930).

† M. Dole, *J. Am. Chem. Soc.*, **53**, 620 (1931).

TABLE I.—MEASUREMENTS OF THE E.M.F. OF A CELL HAVING AN INTERNAL RESISTANCE OF 20 MEGOHMS BY MEANS OF A CONDENSER AND BALLISTIC GALVANOMETER

Potentiometer setting, volts	Time allowed for condenser to charge, sec.	Galvanometer deflections on scale, mm.
0.44	15	L 10.0
0.43	15	L 2.0
0.42	15	R 3.0
0.427	30	L 1.0
0.426	30	L 0.1
0.4258	60	0
0.4258	120	R 0.2
0.4260	120	L 0.2

Accepted potential = 0.4259. L = left; R = right.

Perhaps the most satisfactory indicating device for the measurement of the e.m.f. of a cell with a high internal resistance is the quadrant electrometer. The electrometer is an electrostatic instrument; it measures not current, but potential difference. Its internal resistance is the resistance of an air gap which is considerably greater than the resistance of most e.m.f. cells; hence the quadrant electrometer is generally useful in determining the null point in an e.m.f. measurement. It is not quite so sensitive or so easy to manipulate as a galvanometer; therefore it is advisable to use the galvanometer in measuring the e.m.f. of cells having a low internal resistance. The principle on which the quadrant electrometer (invented by Lord Kelvin) is based is that of the electrostatic attraction existing between bodies charged to different potentials. Imagine a circular box cut into four quarters or quadrants so that there is a small air gap between each quadrant as illustrated in Fig. 3. Opposite quadrants are connected together; one pair is earthed and the other pair is connected to the source of potential difference to be measured. Inside the box formed of the four quadrants hangs the electrometer needle N which is charged to a potential of 90 v.; the other battery lead is earthed. If all four quadrants are at the same potential, the position of the needle will be its mechanical position of rest, but if one pair of quadrants is charged to a certain potential, the needle will swing in a direction depending upon the sign of the charges on the needle and on the quadrants. If D

is the deflection of the needle in units of the scale on which the motion of the light reflected from the suspension mirror is read,

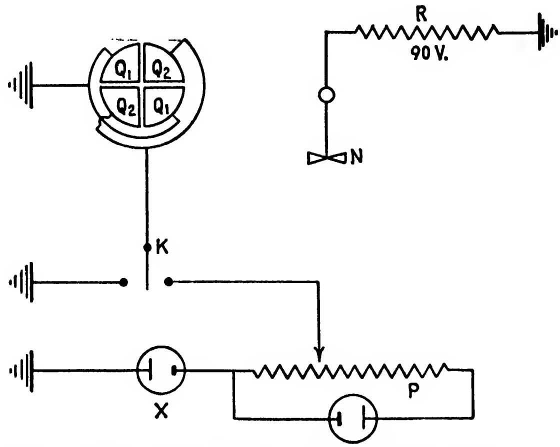


FIG. 3.—Wiring diagram for quadrant electrometer and potentiometer circuit.

and if V and d are the voltages of the needle and of the quadrant pair Q_2, respectively, then

$$D = K_1(2Vd + d^2), \tag{1}$$

where K_1 is a constant. In Fig. 3 P is the potentiometer, X the unknown cell, and K is a special tapping switch so designed that when the instrument is not in use all four quadrants are earthed. Professors A. H. and K. T. Compton* have designed an interesting electrometer in which the needle is tilted about its long axis and one quadrant raised to a height which may be varied, as illustrated in Fig. 4. The purpose of tilting the needle and of controlling the height of one of the quadrants is to be able to vary the electrostatic control over wide limits. By changing the height of the quadrant, the sensitivity of the instrument may be greatly increased. As the sensitivity is increased, the instrument becomes more difficult to work with; hence there are practical limits to the amount the sensitivity may be increased. Other types of electrometers are the Lindemann

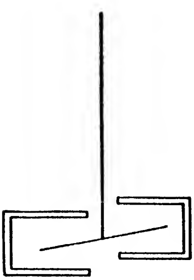


FIG. 4.—Diagrammatic illustration of the tilted needle in the Compton electrometer.

* A. H. and K. T. COMPTON, *Phys. Rev.*, **14**, 85 (1919).

electrometer, capillary electrometer, gold-leaf electrometer, and the string electrometer. The last named is particularly suitable for measuring rapid changes in potential; the fluctuations of the string (which takes the place of the needle) are photographed by a moving-picture camera.

Of late years the vacuum tube has been applied to detect the null point of a potentiometer measurement. Many workers,* among whom may be mentioned Morton, Goode, Fitch, Partridge,

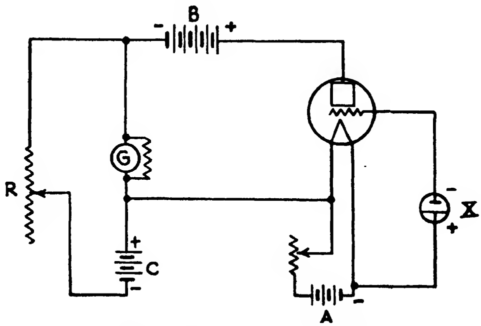


Fig. 5.—The vacuum-tube potentiometer.

Elder, Stadie and Fosbinder, have invented different circuits to accomplish this. The principle of the method is illustrated in Fig. 5 which is a diagram of the original circuit used by Goode. It will be remembered that in a vacuum tube the heat of the filament causes electrons to evaporate from the filament surface; the positive potential of the plate attracts the electrons which flow to the plate through the grid. The filament-plate current which flows through the galvanometer G is a function of the potential of the grid. If the unknown e.m.f. is connected between the grid and the filament, the potential of the grid will be altered and the current flowing through the galvanometer G will

* C. Morton, *J. Chem. Soc.*, **1931**, 2983; Goode, *J. Am. Chem. Soc.*, **44**, 26 (1922); **47**, 2483 (1925); Fitch, *J. Opt. Soc. Am.*, **14**, 348 (1927); H. M. Partridge, *J. Am. Chem. Soc.*, **51**, 1 (1929); L. Elder, *ibid.*, **51**, 3266 (1929); Stadie, *J. Biol. Chem.*, **83**, 477 (1929); R. J. Fosbinder, *J. Phys. Chem.*, **34**, 1294 (1930); L. A. DuBridge, *Phys. Rev.*, **37**, 392 (1931); DuBridge and H. Brown, *Rev. Sci. Inst.*, **4**, 532 (1933); W. Soller, *ibid.*; **3**, 416 (1932); Compton and Haring, *Trans. Electrochem. Soc.*, **62**, 345 (1932); Hill, *Science*, **73**, 529 (1931); Nottingham, *J. Franklin Inst.*, **208**, 469 (1929); **209**, 287 (1930).

be altered. Since the current which flows from the grid to filament is very small, the internal resistance of the cell X may be large without affecting the sensitivity of the method. In the particular circuit used by Goode, the filament-plate current which flowed through the galvanometer in the absence of the unknown e.m.f. was balanced out by an opposite current from the battery C controlled by the variable resistance R. Goode's arrangement is subject to error since at balance or otherwise there is a definite current flowing through the unknown cell X; hence the observed potential will be a function of the internal resistance of X when this becomes high, as Elder has discovered. However, the grid current in the General Electric FP-54 tube is so small that no error of measurement is introduced in its use.

Standard Cells.—In the explanation of the principle of the Poggendorf potentiometer, it was stated that the p.d. of the slide wire *ab* was calibrated by comparison with a known e.m.f., that of the standard cell S of Fig. 1, but nothing was said of the type of cell that can be used as a practical standard. On January 1, 1911, the Bureau of Standards adopted the Weston normal cell as the working standard for the United States.* The Weston normal cell has the following characteristics which make it particularly suitable for a convenient standard: The e.m.f. of the cell has a low temperature coefficient; for a 10° rise of temperature, the e.m.f. of the cell changes −0.5 mv. The equation connecting the e.m.f. with the temperature is

$$E_t = E_{20} - 0.0000406(t - 20) - 0.000{,}000{,}95(t - 20)^2 + 1 \times 10^{-9}(t - 20)^3,$$

where E_{20} equal 1.01830 international volts, the e.m.f. at 20° of the normal cadmium cell, containing saturated solution, when calculated in terms of the international ampere and the international ohm. Other advantages of the Weston cell are low thermal hysteresis, reproducibility, constancy, and long life. The constancy of the cell is due to the fact that no gas is evolved at the negative electrode.

The standard Weston cell is prepared from a 12.5 per cent cadmium amalgam made of pure cadmium dissolved in mercury, cadmium sulfate crystals, saturated cadmium sulfate solution

* *Bur. Standards Bull.*, **4**, 1 (1907); *Bur. Standards Circ.* 29.

as the negative half of the cell; and mercury, insoluble mercurous sulfate, cadmium sulfate crystals, and saturated cadmium sulfate solution as the positive half of the cell.

In actual laboratory practice it is customary to use, instead of the Weston normal standard cell, the Weston secondary standard cell as pictured in Fig. 6.

This working standard cell, which is portable, has its solution saturated with cadmium sulfate at 4°C.; hence at room temperature the cadmium sulfate solution is unsaturated and there are no cadmium sulfate crystals in the cell. The concentration

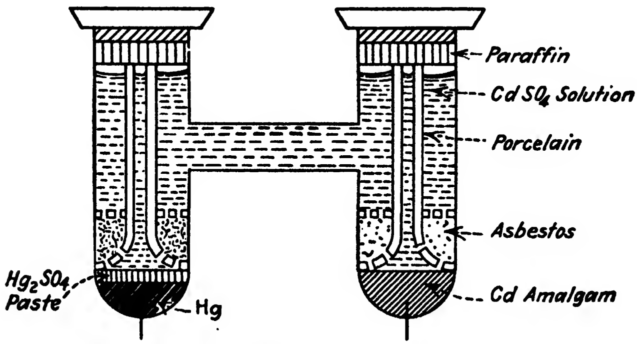


FIG. 6.—The Weston secondary standard cell.

of the solution changes therefore only slightly with the temperature and because of this, the secondary standard cell has a smaller temperature coefficient than the normal standard cell.* In fact, the change of e.m.f. with change of temperature may be neglected. The e.m.f. given by the secondary standard cell is close to 1.0186 v., and its internal resistance is about 200 ohms.

Some Useful Electrodes.—In electrochemistry we are interested in measuring those electrical potentials that give us information concerning chemical processes, and as a large number of chemical reactions take place in solution, it will behoove us to

* Recent publications of papers concerning the Weston standard cell are A. N. Shaw and H. E. Reilley, *Can. J. Research*, **3**, 473–489 (1930); W. C. Vosburgh and K. L. Elmore, *J. Am. Chem. Soc.*, **53**, 2819 (1931); T. C. Poulter, C. Richey, R. Wilson, and J. Fulton, *Proc. Iowa Acad. Sci.*, **36**, 304 (1929); M. F. Malikov, *J. Sci. Instruments*, **7**, 225–228 (1930); G. A. Hulett, *Trans. Am. Electrochem. Soc.*, **58**, 299 (1930).

For precautions in using standard cells, see G. W. Vinal, *Trans. Am. Electrochem. Soc.*, **54**, 255 (1928).

study as carefully and as thoroughly as possible the potentials that are developed between a solution and the following substances, a metal, an insoluble compound, another solution, another liquid phase, semipermeable membranes, quartz, glass, and other "insulators." In carrying out these measurements it is necessary to measure the potential developed at two or more sources, since it is not possible to measure the potential developed at a single source or at a junction of two phases (the single-electrode potential). Consequently most potential measurements consist in measuring the potential difference between the potential desired and the potential of some convenient reference electrode such as the *hydrogen electrode*, the *calomel electrode*, or the *silver chloride electrode.*

The hydrogen electrode consists of simply a square of platinum foil to which electrical connection is made. The platinum is immersed in the solution, through which hydrogen gas is passed. If the solution has a well-defined hydrogen ion concentration and if certain requirements are carefully observed in preparing the electrode, the potential developed between the platinum and the solution is definite and *reproducible.* By reproducibility is meant the ability of several different electrodes to give the same potential. Although there are certain instances where reproducibility of the electrode is not essential, nevertheless in the great majority of e.m.f. cells it can be said that their electrodes must be reproducible for the observed e.m.fs. to have any significance. The hydrogen electrode also gives *reversible* potentials; that is, the potential remains constant even though small currents flow through the electrode in either direction as the e.m.f. is measured. (See the next chapter for a more exact definition of reversibility.) Reversibility and reproducibility are two important conditions that must be met in the preparation of any electrode, and because these conditions are fulfilled in the case of the hydrogen electrode, the hydrogen electrode may be used in e.m.f. cells.

The best form of the hydrogen electrode is a form recommended by Clark.* A piece of platinum foil, 0.08 mm. thick and 1 cm. square, is welded to a wire 0.08 mm. in diameter. The platinum wire lead of the electrode is next sealed into the end of a tube of

* W. M. Clark, "The Determination of Hydrogen Ions," Chap. XIV, Williams & Wilkins Company, Baltimore, 1928.

soft glass, and the glass allowed to flow down onto the platinum foil to secure the electrode firmly to the glass tube. The steps of this process are illustrated in Fig. 7.

The smooth, bright platinum surface must be covered with a layer of platinum black in order that the electrode reaction (*i.e.*, the reaction when the current is passed)

$$2H^+ + 2\epsilon^- \rightleftarrows 2H \rightleftarrows H_2$$

may proceed reversibly. Platinum black is platinum in a colloidal condition and has the ability to sorb or dissolve gaseous hydrogen and hydrogen ions, thereby allowing the above reaction to take place under the optimum conditions. There are many other methods for preparing hydrogen electrodes including the use of gauze or film electrodes, platinum and palladium

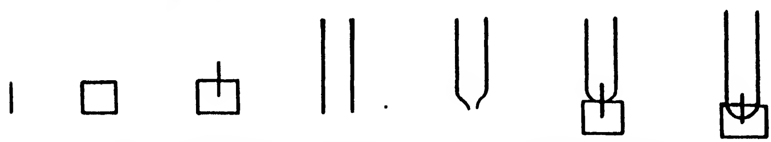


FIG. 7.—Steps in the preparation of the hydrogen electrode.

black deposited on gold, thin or thick surfaces of platinum black, etc.*

The hydrogen which is bubbled through the solution over the platinum electrode must be carefully purified. It is most convenient to have a tank of commercial hydrogen as the source of the hydrogen; the only impurity of consequence that must be removed is oxygen. Guntelberg† recommends that the oxygen be removed by passing the hydrogen over catalytic copper heated to a temperature of 450°C. The copper surface is conveniently obtained by reducing copper oxide, in wire form, in a quartz or pyrex glass tube. If the surface is not active on the first reduction, it can be reoxidized and reduced several times until the surface has become catalytically active.‡

Another electrode which is widely used as a reference electrode is the *calomel* electrode or calomel half cell. The calomel elec-

* The reader is referred to the excellent treatise, "The Determination of Hydrogen Ions," by W. Mansfield Clark, for further details.

† E. GUNTELBERG, *Z. physik. Chem.*, **123**, 199 (1926).

‡ See also D. A. MACINNES and I. A. COWPERTHWAITE, *J. Am. Chem. Soc.*, **53**, 555 (1931).

trode consists of mercury covered with a layer of insoluble mercurous chloride (calomel) which is in equilibrium with a solution of potassium chloride saturated with the calomel. The concentration of the potassium chloride may be 0.1 *N*, 1.0 *N*, or saturated, and half cells containing potassium chloride solutions of these concentrations are commonly referred to as "tenth normal," "normal" or "saturated calomel electrodes." A convenient vessel for holding the mercury, calomel and solution is illustrated in Fig. 8. Electrical contact to the mercury of the half cell is made by means of the platinum wire sealed

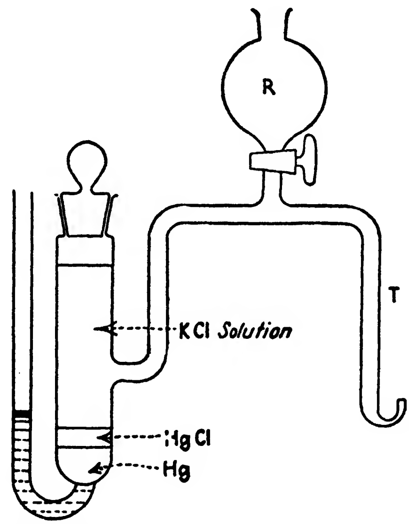


FIG. 8.—A convenient form of the calomel half cell.

through the pyrex glass (pyrex may be used here because the sealed-in wire is covered by mercury on both sides of the seal). The reservoir *R* contains potassium chloride solution to flush out the glass tube *T* which connects the half cell with any desired solution. If the potassium chloride solution is saturated, the tip of *T* is turned up, but if it is a 1.0 *N* or 0.1 *N* solution and if *T* then dips into a saturated potassium chloride solution, the tip of *T* is not turned up. The mercury should be purified by spraying through a tower of dilute nitric acid followed by distillation in a slow stream of air. Final distillation *in vacuo* is also to be recommended. The calomel can be made by dissolving

excess of mercury in purified nitric acid and then adding purified hydrochloric acid. The precipitated calomel must be washed repeatedly by decantation. Sometimes the calomel is made by the electrolysis of mercury in 1.0 N hydrochloric acid. Direct current causes the mercurous ions to pass into solution where they precipitate with the chloride ions as mercurous chloride. The electrolysis method provides an intimate contact between the mercury and the calomel, which is desirable. The calomel is sometimes shaken with mercury to obtain an intimate mixture.

The calomel electrode reaction is

$$2Hg + 2Cl^- \rightarrow Hg_2Cl_2 + 2\epsilon^-.$$

The so-called "silver chloride" electrode is similar in principle to the calomel electrode, but is more compact and can be used in certain experiments where it is inconvenient to use the calomel electrode.* Jones and Hartmann† have described a silver iodide electrode. Their method of making the silver iodide electrode may be used to make the silver chloride electrode. The Jones and Hartmann electrode is illustrated in Fig. 9. It is built on a platinum wire which is sealed into a tube of soft glass. The platinum wire is silver-plated from a silver cyanide bath and after washing,‡ the coil of silver-plated platinum is covered with a large mass of purified silver oxide. By heating to 325°C. the silver oxide is reduced to metallic silver; in this way a mass of spongy silver having a comparatively large surface is obtained in a small bulk. The silver electrode is finally made the anode in a solution of approximately 0.1 N sodium chloride, and on passing a low current, 0.001 amp., through the cell for several

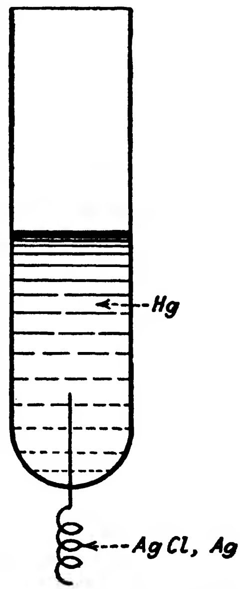


FIG. 9.—The Jones and Hartmann form of the silver halide electrode.

* As the reference electrode inside the MacInnes and Dole glass electrode, for example.

† GRINNELL JONES and M. L. HARTMANN, *J. Am. Chem. Soc.*, **37**, 752 (1915).

‡ W. R. Carmody, *J. Am. Chem. Soc.*, **51**, 2901 (1929), recommends washing in running water for five days in order to obtain *white* silver chloride in the subsequent electrolysis. See also A. S. Brown, *ibid.*, **56**, 646 (1934).

hours, silver chloride is formed on the electrode. The electrode reaction is

$$Ag + Cl^- \rightleftarrows AgCl + \epsilon^-,$$

hence it is evident that the silver chloride electrode should only be used in a solution that has a well-defined chloride ion concentration. Several electrodes made at the same time will give the same e.m.f. between each other with deviations of only a few hundredths of a millivolt.

Exercises

1. What are the electrode reactions at each electrode of the Weston standard cell during passage of the current?
2. Suggest a form for a silver halide electrode which is different from the Jones and Hartmann type.
3. Draw a wiring diagram for a potentiometer-condenser-ballistic galvanometer circuit.

CHAPTER XV

FUNDAMENTALS OF THERMODYNAMICS

Reversible and Irreversible Processes.—In our study of electrolytic conductances, transference numbers, and dielectric constants we were not particularly interested in the energy relationships involved because all the phenomena considered were essentially irreversible in nature, *i.e.*, the energy imparted to a system to bring about a desired change could not all be recovered by allowing the system to return to its original state. In conductance measurements a certain amount of energy necessary to overcome the viscous friction of the medium is required to move an ion from one position to another. This energy is irreparably lost since it cannot be regained by returning the ion to its original position, in fact still more energy must be expended to bring this about. In transference measurements some of the added energy is indeed stored up in the system, but some is also lost in the same manner that energy is lost in conductance measurements; hence the process of electrolytic transference is also irreversible. A perfect condenser would discharge as much electricity as had flowed into it, and would, therefore, act reversibly. But no practical condenser is a perfect condenser; there are always some energy losses in the dielectric.

In order for a process to be strictly reversible it must consist of a series of changes between a number of states, each state of which must be a state of equilibrium. At every point of a reversible process the system is in so perfect a balance that it would require only an infinitesimal change in the external conditions to cause a reversal in the direction of the process. A reversible process must consist of an infinitesimal change or it must be a large change carried out infinitely slowly. Practically it is never possible to carry out a process in either of these ways; nevertheless the measurement of the e.m.f. of a galvanic cell approximates a truly reversible process very closely, for the driving force of the e.m.f. is balanced against the p.d. of the

potentiometer in such a way that the current flowing through the cell may be made to reverse its direction by only a minute change of the voltage of the potentiometer. In fact, in the most favorable cases a change in the direction of the current may be detected by a voltage change of only one millionth of a volt. When the p.d. of the potentiometer is balanced against the e.m.f. of the galvanic cell, no current flows through the cell; hence no energy is dissipated due to the electrical resistance of the solution to the current.

Because of the reversibility of the process of measuring the e.m.f., we can apply the principles and equations of thermodynamics in the interpretation of the measured values, and so gain more valuable chemical information than we could if the e.m.f. measurements were not reversible in nature. Thermodynamics is an exact science; the rigor of its equations makes possible a clear and logical correlation and systematization of the data in a manner whose accuracy cannot be questioned. Before discussing in detail the thermodynamics of electrochemical cells, we shall devote this chapter to a brief introduction to those fundamental relations of thermodynamics which we shall find of use in later chapters.

The First Law of Thermodynamics.—The first law of thermodynamics is applicable to any process, reversible or irreversible, because it is a mathematical statement of the fundamental postulate that in any chemical reaction which occurs in an isolated system energy is conserved. There is no net gain or loss of energy, although there may be conversion of one form of energy into another. The mathematical expression of the first law as applied to an infinitesimal change in the system is

$$dU = w + q. \tag{1}$$

Equation (1) states that the increase in energy of the system dU is equal to the heat *gained* by the system q plus the work done *on* the system w.* The first law of thermodynamics need not be

* The thermodynamic symbols and conventions adopted here are the same for the most part as those used by Guggenheim in his recent book entitled "Modern Thermodynamics by the Methods of Willard Gibbs," Methuen and Co., London, 1933. His symbol for energy, E, will be replaced here by the European symbol, U, since we have already defined E as meaning voltage and e.m.f. Other textbooks of thermodynamics are "Thermo-

restricted to an infinitesimal change; in the case of a finite process we write

$$\Delta U = w + q, \tag{2}$$

where ΔU is the difference in energy of the system between the final and initial states. The absolute value of U is not known; it is only a change in U which we can measure and which has thermodynamic significance. Furthermore, the value of ΔU depends only upon the values of U for the initial and final states of the system and is independent of the path by which the system passes from the initial to the final state.

The Second Law of Thermodynamics.—The second law of thermodynamics is most concisely expressed by means of a function called entropy and denoted by the symbol S. For an infinitesimal, isothermal and reversible process, the quantity of heat absorbed from the surroundings divided by the absolute temperature defines the entropy change

$$\frac{q}{T} = dS. \tag{3}$$

Clausius stated the second law by saying that the entropy of the world tends to increase to a maximum. The second law may also be stated by saying that the entropy of a system is proportional to the logarithm of its probability. The physical significance of these statements is that in an irreversible spontaneous process the entropy change is greater than

$$\frac{q}{T_{max.}}$$

where $T_{max.}$ is the maximum value of the temperature in any part of the system. For a reversible cycle which leaves the system in the same state as its initial state, the entropy change is zero. Like the absolute value of the energy, the absolute value of the

dynamics and the Free Energy of Chemical Substances," by G. N. Lewis and M. Randall, McGraw-Hill Book Company Inc., New York, 1923; 'Thermodynamics and Chemistry," by F. H. MacDougall, John Wiley & Sons, Inc., New York, 1926; "The Collected Works of J. Willard Gibbs," Vol. I, Longmans, Green & Co., New York, 1928; "A Treatise on Physical Chemistry," Chap. XII, by H. S. Harned, D. Van Nostrand Company, New York, 1931.

entropy has no meaning; it is only a change in entropy that has thermodynamic significance.

An important corollary of the second law of thermodynamics is the Carnot cycle which was developed by Carnot in 1824, about 25 years before Kelvin defined the absolute scale of temperature and about 25 years before Clausius clearly enunciated the second law. Let us consider a system in good thermal contact with a large heat reservoir, all at the temperature T_1. The first step in the cycle, which is made up of four steps, consists in the reversible absorption of heat q_1. Since this absorption of heat takes place without any change of temperature, it is an *isothermal* process. The system is now removed from contact with the heat reservoir and by some process such as expansion, the temperature is allowed to fall reversibly to a lower temperature, T_2. Since this second step occurs without gain or loss of heat, the process is an *adiabatic* process and the entropy change in the process is equal to zero. The third step in the cycle consists in the isothermal transfer of heat between the system and a large heat reservoir at the temperature T_2 with which the system is now in good thermal contact. The last step is an adiabatic reversible change from temperature T_2 to T_1 which restores the system to its original state. The energy and entropy of the system now being the same as in the original state, we can say that

$$\Delta S = 0 \tag{4a}$$

$$\Delta U = 0. \tag{4b}$$

The entropy changes in the four steps may now be added together and set equal to zero; thus

$$\frac{q_1}{T_1} + 0 + \frac{q_2}{T_2} + 0 = 0, \tag{5}$$

or

$$\frac{q_1}{T_1} = \frac{-q_2}{T_2}. \tag{6}$$

But from Eqs. (4) and (2),

$$q + w = 0, \tag{7}$$

and

$$w = -(q_1 + q_2);$$

Hence

$$w = -q_1\frac{(T_1 - T_2)}{T_1}. \tag{8}$$

Equation (8) is of great importance in engineering because it states that the work which may be obtained from the quantity of heat absorbed, q_1, is proportional to $\frac{T_1 - T_2}{T_1}$.

Of more importance to electrochemistry are the thermodynamic functions, H, the heat content, and G, the free energy.*

The Heat Content, the Free Energy, and the Equation of Gibbs and Helmholtz.—In most chemical experiments, in calorimetry and in electrochemistry, the pressure of the system remains constant while the volume varies. When we measure the energy change in a reaction by measuring the heat absorbed by the system from its surroundings, we must take into consideration the fact that the volume of the system may change and the surroundings in this way may do work on the system. If the pressure is kept constant, the work done on the system will be equal to $-P\Delta V$, where ΔV is the volume change of the system during the reaction. From Eq. (2) we have then

$$\Delta U = q - P\Delta V$$

or

$$\Delta U + P\Delta V = q. \tag{9}$$

By analogy with Eq. (9) let us define the heat content H by the equation

$$H = U + PV. \tag{10}$$

The quantity H, like the quantities U and S, depends only on the state of the system and is independent of the previous history of the system. A change in H, therefore, is determined solely by the initial and final states of the system and is not necessarily limited to the condition of constant pressure.†

* The symbol G of this book has the same meaning as the symbol F of Lewis and Randall.

† The utility of the heat-content function is aptly illustrated by the Joule-Thomson experiment in which a mole of gas having the energy content U, the volume V, and the pressure P is passed adiabatically through a porous plug so that its energy content is now U', its volume V', and its pressure P'. Since q is zero (adiabatic process), and since PV-$P'V'$ is equal to w

$$U + PV = U' + P'V'$$

or

$$H = H'. \tag{11}$$

The Joule-Thomson experiment is, therefore, a process occurring at constant H.

As shall be emphasized in the next chapter, we are chiefly interested in the maximum amount of work which may be obtained in any given process, or we are interested in what might be called the available energy contained in a system. This available energy is usually called the "free energy" and may be defined in several different ways. The free energy G, called by Guggenheim the "Gibbs free energy," is defined by the equation

$$G = H - TS. \tag{12}$$

The electrochemical significance of the free energy will be discussed in detail in the next chapter.

Differentiating Eq. (12) we have

$$dG = dH - TdS - SdT. \tag{13}$$

If we restrict ourselves to a change in a reversible process, we can substitute TdS for q and $-PdV$ for w in Eq. (1), obtaining

$$dU = TdS - PdV. \tag{14}$$

Differentiating Eq. (10),

$$dH = dU + PdV + VdP, \tag{15}$$

and combining with Eq. (14), we obtain

$$dH = TdS + VdP. \tag{16}$$

Eliminating dH from Eqs. (16) and (13) the equation

$$dG = VdP - SdT \tag{17}$$

results. The free-energy change at constant pressure is, therefore,

$$\left(\frac{dG}{dT}\right)_P = -S. \tag{18}$$

Rearranging Eq. (12),

$$\frac{G - H}{T} = -S$$

and combining with Eq. (18), we have

$$G - H = T\left(\frac{dG}{dT}\right)_P, \tag{19}$$

which is called the Gibbs-Helmholtz equation. Since only *changes* in free energy and changes in heat content have thermodynamic significance, it is better to write Eq. (19) as

$$\Delta G - \Delta H = T\left(\frac{d\Delta G}{dT}\right)_P. \tag{20}$$

Equation (20) is a very important and useful equation for it enables us to calculate the heat-content change if both the free-energy change and its temperature coefficient are known.

Equilibrium and Stability.—Systems when left to themselves tend to approach states of minimum energy. Thus a stone will roll down a hill if possible to a position of smaller potential energy. An atom in a state of high-energy content will spontaneously revert if possible to a state of lower energy content by emitting energy in the form of radiation. In Fig. 1 the energy of a system is plotted along the y-axis and some function r, such as distance between two parts of the system along the x-axis. As r decreases, the energy will decrease until the point A is reached when a further decrease of r causes an increase in the energy. The point A represents a position of stability insofar as infinitesimal variations of r are concerned, $\partial U/\partial r = 0$. However, the position represented by A is unstable in reference to the position represented by the point B.

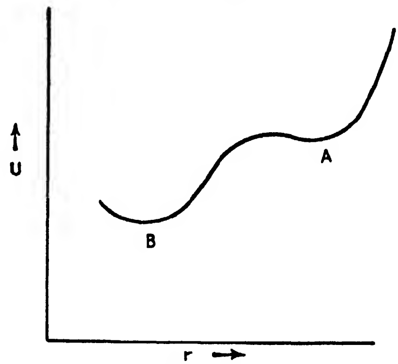


FIG. 1.

Let us consider a reversible infinitesimal change taking place in a system thermally insulated. Since the change under these conditions is adiabatic, q is equal to zero, and by Eq. (1)

$$dU = w, \qquad dS = 0. \tag{21}$$

If the process occurs at constant volume, w is equal to zero and we have

$$dU = 0, \qquad dV = 0, \qquad \text{and} \qquad dS = 0. \tag{22}$$

If the system is in complete equilibrium, every conceivable infinitesimal change in it must be reversible; but Eqs. (22) were derived on the assumption of a reversible change. They represent, therefore, conditions of equilibrium. If we consider an

infinitesimal change at constant pressure and constant temperature, the equilibrium conditions become

$$dT = 0, \qquad dP = 0, \qquad dG = 0. \tag{23}$$

The work done on the system in this case is

$$-PdV = -d(PV). \tag{24}$$

But from Eq. (10) we have

$$dH = dU + d(PV) \tag{25}$$

and from Eq. (12) we have

$$dG = dH - TdS \tag{26}$$

or

$$dG = dU + d(PV) - TdS. \tag{27}$$

But

$$dU = w + q = -d(PV) + TdS \tag{28}$$

for a reversible process; hence

$$dG = 0$$

in agreement with Eqs. (23). The equilibrium conditions as given by Eqs. (23) are of the greatest practical importance since most e.m.f. measurements are carried out under conditions of constant temperature and pressure.

The Chemical Potential.—Up to this point we have been tacitly making the assumption that all the changes described above were changes taking place in a single phase without any alteration of composition. Following the treatment given by Guggenheim, we may generalize our equations by regarding the energy as a function not only of the volume and entropy, but also of the composition, or

$$dU' = \left(\frac{dU'}{dS'}\right)_{V',n_i'} dS' + \left(\frac{dU'}{dV'}\right)_{S,n_i'} dV' + \sum_i \left(\frac{dU'}{dn_i'}\right)_{S,V',n_j'} dn_i'. \tag{29}$$

Equation (29) states that the total change in the energy is the sum of the changes in energy due to the changes in entropy, volume, and composition. The primes restrict the symbols to a single phase and n_j denotes all quantities of the type n_i except n_i itself. The unit of n_i may be considered the mole, different n_i's represent different chemical components of the phase. Assuming T and P constant and constant composition, Eq. (28) becomes

$$dU = TdS - PdV. \tag{30}$$

If the composition of the phase is constant, Eq. (29) may be written

$$dU' = \left(\frac{dU'}{dS'}\right)_{V',n_i'} dS' + \left(\frac{dU'}{dV'}\right)_{S',n_i'} dV'. \tag{31}$$

From Eqs. (31), (30), and (29) we have the equation

$$dU' = T'dS' - P'dV' + \Sigma_i \mu_i' dn_i', \tag{32}$$

where

$$\mu_i' = \left(\frac{dU'}{dn_i'}\right)_{S',V',n_j'}, \tag{33}$$

$$T' = \left(\frac{dU'}{dS'}\right)_{V',n_i'}, \tag{34}$$

and

$$P' = \left(\frac{dU'}{dV'}\right)_{S',n_i'}. \tag{35}$$

Equation (32) was first derived by Gibbs. The function μ is called the chemical potential.

Differentiating Eq. (12),

$$dG' = dU' + P'dV' + V'dP' - T'dS' - S'dT', \tag{36}$$

and eliminating dU by means of Eq. (32), we have

$$dG' = V'dP' - S'dT' + \Sigma_i \mu_i' dn_i', \tag{37}$$

or at constant temperature and pressure

$$\mu_i' = \left(\frac{dG'}{dn_i'}\right)_{P',T',n_j'}. \tag{38}$$

Thus, the chemical potential may be defined in terms of the free energy at constant temperature and pressure.

To understand in part the significance of chemical potential let us now follow Gibbs* and consider a system containing several phases in equilibrium. To simplify matters we shall assume that the phases in contact are uninfluenced by gravity, electricity, distortion of the solid phases, and that the surfaces of contact between the phases are plane. The components will

* J. W. Gibbs, "Collected Works," Vol. I, pp. 62–66. Longmans, Green and Co., New York, 1928.

be independently variable; this restriction eliminates ions from our consideration [Eq. (32) holds for ions]. Later on we shall describe the types of equilibria into which ions may enter. The various components must also be free to move between the phases.

Our equilibrium conditions (22) state that at equilibrium dU, dS and dV are zero. If the system is isolated, dn_1, dn_2, etc., are also zero. However, there may be individual variations between the phases allowing us to write the equations,

$$\delta U' + \delta U'' + \delta U''' \cdots = dU = 0 \tag{39a}$$
$$\delta S' + \delta S'' + \delta S''' \cdots = dS = 0 \tag{39b}$$
$$\delta V' + \delta V'' + \delta V''' \cdots = dV = 0 \tag{39c}$$
$$\delta n_1' + \delta n_1'' + \delta n_1''' \cdots = dn_1 = 0 \tag{39d}$$
$$\delta n_2' + \delta n_2'' + \delta n_2''' \cdots = dn_2 = 0 \tag{39e}$$
$$\text{etc.}$$

$\delta U'$ is the variation of the energy in the first phase, $\delta U''$ in the second phase, etc. For the above equations to be true it is necessary and sufficient that

$$T' = T'' = T''' \cdots \tag{40a}$$
$$P' = P'' = P''' \cdots \tag{40b}$$
$$\mu_1' = \mu_1'' = \mu_1''' \cdots \tag{40c}$$
$$\mu_2' = \mu_2'' = \mu_2''' \cdots \tag{40d}$$
$$\text{etc.}$$

Equations (40*a*) and (40*b*) express that, at equilibrium the temperature and pressure are constant throughout the whole mass —a fact that is easily realized and understood. Equations (40*c*) and (40*d*) tell us that, at equilibrium the chemical potentials of the various components must also be constant throughout the mass; in other words, we have chemical equilibrium as well as thermal and mechanical equilibrium when the whole system is in equilibrium. The importance in electrochemistry of the relationships (40*c*) and (40*d*) will be more clearly realized in the chapter on semipermeable-membrane and phase-boundary potentials.

Free Energy and Pressure, Chemical Potential, and Fugacity. A perfect gas expanding at constant temperature suffers no change in energy. Its kinetic energy at constant temperature is constant. If the gas does external work by expansion, the energy

which is converted into work must be absorbed in the form of heat from the surroundings, or

$-w = q$ (provided there is no dissipation of energy due to friction).

The work done on the system, w, is $-PdV$, hence

$$-w = PdV. \tag{41}$$

For a finite change in the volume w becomes

$$w = -\int_{V_A}^{V_B} PdV,$$

and on substituting for P from the gas law,

$$w = -nRT \ln \frac{V_B}{V_A} = nRT \ln \frac{P_B}{P_A}, \tag{42}$$

where n is the number of moles. Let us now derive an expression similar to Eq. (42) for the relation between the free energy of a perfect gas and its pressure.*

The definition of the free energy G is given by the equation

$$G = H - TS. \tag{12}$$

Differentiating Eq. (12) with respect to pressure at constant temperature,

$$\left(\frac{dG}{dP}\right)_T = \left(\frac{dH}{dP}\right)_T - T\left(\frac{dS}{dP}\right)_T. \tag{43}$$

From Eq. (16) we have

$$\left(\frac{dH}{dP}\right)_T - T\left(\frac{dS}{dP}\right)_T = V, \tag{44}$$

and combining Eqs. (44) and (43),

$$\left(\frac{dG}{dP}\right)_T = V$$

or

$$\int G = \int VdP. \tag{45}$$

Introducing the perfect gas law as before and integrating,

$$G_B - G_A = nRT \ln \frac{P_B}{P_A}. \tag{46}$$

* See LEWIS and RANDALL, "Thermodynamics," p. 162. McGraw-Hill Book Company, Inc., New York, 1923.

At constant temperature and pressure

$$\left(\frac{dG}{dn}\right)_{P,T} = \mu \tag{38}$$

hence we may write Eq. (46) in terms of the chemical potential,

$$\mu_B - \mu_A = RT \ln \frac{P_B}{P_A}. \tag{47}$$

The chemical potential, it should be noted, is identical with the partial molal free energy of Lewis and Randall.

Equation (47) is valid for a perfect gas; for a nonperfect gas Lewis* introduces a function called the "fugacity," defined by the equation

$$\mu = \mu^\circ + RT \ln P^*, \tag{48}$$

where μ° is a function of the temperature only, and P^* is the fugacity. Between two isothermal states we may write

$$\mu_B - \mu_A = RT \ln \frac{P_B^*}{P_A^*}, \tag{49}$$

or for an infinitesimal change

$$d\mu = RTd \ln P^*. \tag{50}$$

Dilute Solutions and the Activity Coefficient.—Of greatest importance and usefulness in electrochemistry are the thermodynamical laws of the dilute solution and relationships based on these laws either formally or by analogy.

A unit of concentration which is most commonly used in thermodynamics is the mole fraction. If a solution is composed of two components, A and B, the mole fraction of A is defined as the number of moles of A divided by the total number of moles of A and B, or

$$N_A = \frac{n_A}{n_A + n_B}.$$

In general

$$N_i = \frac{n_i}{\Sigma_k n_k}. \tag{51}$$

In Eq. (51) n_i is the number of moles of the ith component and N_i is its mole fraction. $\Sigma_k n_k$ is the sum over all species.

* G. N. Lewis, *Proc. Am. Acad.*, **37**, 49 (1901).

Lewis and Randall* point out that from one assumption all the laws of the dilute solution may be deduced. This assumption is that if p_2^*, the fugacity of the solute, is plotted against N_2 its mole fraction, the slope of the curve, dp_2^*/dN_2, at the point $N_2 = 0$ is finite. Since

$$\frac{dy}{dx} = \frac{y}{x}$$

in the neighborhood of the point where $x = 0$ and $y = 0$, it follows from our assumption that

$$\frac{\partial p_2^*}{\partial N_2} = \frac{p_2^*}{N_2} = \text{const.}$$

or

$$p_2^* = kN_2. \tag{52}$$

This is similar to Henry's law

$$p_2 = kc, \tag{53}$$

where p_2 is the vapor pressure of the solute and c is its concentration. Equations (52) and (53) coincide at infinite dilution where p_2^* equals p_2. Deviations from Henry's law at finite concentrations may be due to the fact that the vapor of the solute no longer behaves as a perfect gas, or that the fugacity of the solute is no longer proportional to its mole fraction.

Equation (50) is also valid for the fugacity of a solute; thus,

$$d\mu_2 = RTd \ln p_2^*. \tag{54}$$

Eliminating the fugacity from Eqs. (52) and (54), we have

$$d\mu_2 = RTd \ln N_2 \tag{55}$$

or in general

$$\mu_i = \mu_i^\circ + RT \ln N_i, \tag{56}$$

where μ_i° depends upon the temperature and pressure but not upon the composition. Equation (56) is valid as long as Eq. (52) is valid, but strictly speaking Eq. (56) is valid only at zero concentration, $N_i = 0$.

* "Thermodynamics," p. 232.

We can generalize Eq. (56), however, by introducing a function f, first defined by G. N. Lewis (Lewis actually defined γ, not f; see below) and called the activity coefficient; thus

$$\mu_i = \mu_i^\circ + RT \ln N_i f_i. \tag{57}$$

Equation (57) is valid for any component of any solution; the constant μ_i° for a given solvent is solely a function of the temperature and pressure. The activity coefficient f_i has the property of equaling unity when N_i equals zero if N_i refers to the solute. If N_i refers to the solvent, then f_i equals unity when N_i equals unity. In other words, the activity coefficient of the solvent and solute both equal unity in the pure solvent (by definition).

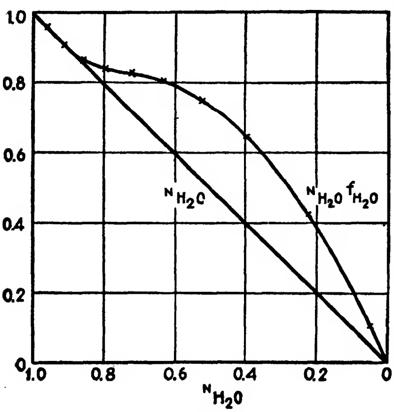


FIG. 2.

The activity coefficient and Eq. (57) are very important as far as electrochemistry is concerned. In order to illustrate the meaning of the activity coefficient, the activity coefficient of water in alcohol-water mixtures is plotted in Fig. 2 as a function of the mole fraction of the water, or rather values of $N_{H_2O} f_{H_2O}$ are so plotted.* Values of N_{H_2O} are also plotted and it is readily seen that the mole fraction of the water is less over nearly the whole range than the $N_{H_2O} f_{H_2O}$ values. Speaking in terms of the chemical potential, we say that the chemical potential of water in alcohol-water mixtures is much higher than we would expect on the basis of the behavior of a perfect solution.

The Mass Action Law.—It is necessary to consider one more important relation before leaving the subject of thermodynamics. If the reaction

$$aA + bB \rightleftarrows cC + dD \tag{58}$$

is in equilibrium, for any infinitesimal change such as

$$\delta aA + \delta bB \rightarrow \delta cC + \delta dD \tag{59}$$

* Lewis and Randall call $N_i f_i$ the "activity." "Thermodynamics," p. 255.

the free-energy change, dG, will be equal to zero (temperature and pressure assumed to be constant). From Eq. (37)

$$dG = VdP - SdT + \Sigma_i \mu_i dn_i; \tag{37}$$

hence for the reaction (52), it is true that

$$\delta a\mu_A + \delta b\mu_B = \delta c\mu_C + \delta d\mu_D$$

or

$$a\mu_A + b\mu_B = c\mu_C + d\mu_D. \tag{60}$$

For the values of the chemical potential in Eq. (60) let us substitute the values given by Eq. (56). After rearranging we obtain

$$\begin{aligned} a\mu_A^\circ + b\mu_B^\circ - c\mu_C^\circ - d\mu_D^\circ &= \text{const.} \\ &= RT \ln \frac{(N_C f_C)^c \cdot (N_D f_D)^d}{(N_A f_A)^a \cdot (N_B f_B)^b}, \end{aligned} \tag{61}$$

or

$$\frac{(N_C f_C)^c \cdot (N_D f_D)^d}{(N_A f_A)^a \cdot (N_B f_B)^b} = K, \tag{62}$$

where K is a constant depending only on the solvent, temperature, and pressure. Since

$$c\mu_C^\circ + d\mu_D^\circ - a\mu_A^\circ - b\mu_B^\circ = \Delta G^\circ, \tag{63}$$

where ΔG° is the free energy of the reaction (58) when the reaction occurs between reactants in the state, $\mu = \mu^\circ$ to give products in the state, $\mu = \mu^\circ$, we can write

$$\Delta G^\circ = -RT \ln K. \tag{64}$$

Equation (64) is an important equation because it enables us to calculate the mass action constant of a reaction if ΔG° is known. We can calculate ΔG° from e.m.f. measurements in certain favorable cases.

From Eq. (57) it is obvious that the state $\mu = \mu^\circ$, called the **standard state,** is the state of the solution when $N_i f_i$ is equal to unity. In the words of Lewis the standard state is the state of unit activity.

CHAPTER XVI

THE THERMODYNAMICS OF CELLS WITHOUT LIQUID JUNCTIONS

Electromotive Force and Free Energy.—In the last chapter we were interested chiefly in collecting together and deriving mathematically and briefly the more important thermodynamic functions. It is the purpose of this chapter to give some physical significance to these functions and to illustrate their usefulness in interpreting the results of electromotive force measurements. As the first example of an e.m.f. cell let us choose a cadmium and hydrogen cell which was studied at the early date of 1869 by the Frenchman Favre.* The results of Favre are particularly interesting historically because they are described and discussed by Gibbs in his famous memoir "On the Equilibrium of Heterogeneous Substances," and no doubt helped Gibbs† to arrive at his understanding of the energy relations in the galvanic cell.

Favre immersed a cadmium electrode and platinum electrode in a solution of hydrochloric acid so that the following cell was set up,

$$-\mathrm{Cd} \mid \mathrm{HCl} \mid \mathrm{H_2, Pt} +. \qquad (A)$$

In writing down an e.m.f. cell it is customary to represent boundaries between phases by single vertical lines. In cell (A) there is a phase boundary between the cadmium electrode and hydrochloric acid and between the hydrochloric acid and the platinum electrode. The symbol H_2, Pt signifies that hydrogen gas is in contact with the platinum electrode; for the sake of convenience we shall consider the combination of H_2, Pt as representing a single metallic phase. If an e.m.f. cell contains in addition to phase boundaries a boundary between two miscible phases such as a junction between 0.1 and 0.01 N hydrochloric acid, the cell is called an

* P. A. Favre, *Compt. Rend.*, **68**, 1305 (1869).

† "The Collected Works of J. W. Gibbs," Vol. I, pp. 338–349, Longmans, Green & Co., New York, 1928.

e.m.f. cell with liquid junction and the liquid junction is represented by a pair of vertical lines. We shall not consider cells of this type in this chapter, but shall describe here cells without a liquid junction such as cell (*A*).

Cadmium is more active than hydrogen, as every student of freshman chemistry knows, and will tend to displace hydrogen from solution. If the cadmium and platinum electrodes of cell (*A*) are connected by a metallic conductor, a current will flow in such a direction that the following reaction will take place in the cell:

$$Cd + 2HCl \rightarrow CdCl_2 + H_2.$$

At the cadmium electrode ions will dissolve and at the platinum electrode hydrogen ions will be discharged, forming hydrogen gas. If we measure the e.m.f. of the cell by means of a potentiometer, the platinum electrode will be the positive electrode and the cadmium electrode will be the negative electrode. Inside the cell chloride ions will migrate toward the cadmium electrode, while in the metallic connection outside the cell negative electrons will flow away from the cadmium electrode. For this reason we might call the cadmium electrode the negative electrode if we consider the motion of electricity in the metallic connection or we might call it the positive electrode if we consider the motion of electricity inside the cell.* We choose to call the cadmium electrode the negative electrode, in fact, we shall always give the electrodes the sign which is actually measured by a potentiometer. Other conventions† adopted are:

1. The cell will always be written down so that positive electricity flows through the cell from left to right (as one reads).

2. The right-hand electrode will be the positive electrode except in one or two minor cases which will be pointed out.

3. The potential difference of a cell or the e.m.f. will be taken as positive except in one or two minor cases which will be pointed out.

In order to determine the energy relationships of his cadmium-hydrogen cell Favre replaced the metallic connection between

* The names anode and cathode should not be applied to the electrodes of an e.m.f. cell.

† It will be necessary to introduce additional conventions when considering standard electrode potentials.

the two electrodes by a resistance. He then placed both the cell and the resistance in the same calorimeter and found that 7,968 cal.* of heat were evolved when the current had passed through the cell long enough to liberate 1 g. of hydrogen (1 faraday of electricity). Favre next measured the heat evolved solely by the resistance as one faraday of electricity passed through the cell and found this quantity to be 9,256 cal. This result astounded Favre and led him to postulate side reactions taking place in the cell, reactions which absorbed heat. However, no side reactions have ever been discovered, nor is it necessary any longer to postulate their existence. Gibbs was able to explain Favre's data purely on the basis of thermodynamics. The calculations which Gibbs made will be described now, but it must be remembered that these calculations are only approximate due to the fact that Favre did not measure the e.m.f. of a strictly reversible reaction and that the internal resistance of his cell was necessarily neglected in the calculations.

Referring to Eq. (XV-2) it is evident that the increase of internal energy of the cell is equal to the heat added to the system plus the work done on the system, or conversely, the decrease of internal energy, $-\Delta U$, is equal to the heat evolved by the system, $-q$, plus the work done by the system, $-w$. If we neglect work done against gravity, the work done by the galvanic cell will be equal to the electrical work done by the cell plus the work done by the cell by the hydrogen being evolved against the pressure of the atmosphere. The electrical work done by the cell, $-w_e$, is equal to the number of coulombs of electricity passed through the cell multiplied by the e.m.f. or

$$-w_e = EnF, \tag{1}$$

where E is the e.m.f. and n is the number of faradays. The unit of energy in the calculation of electrical work is the joule, but joules may be converted to calories by dividing the number of joules by 4.182. The value of $-w_e$ or of EnF was determined by Favre by measuring the electrical energy liberated as heat energy in the resistance external to the cell. As related above this value was found to be 9,256 cal. The work done by the system due to the evolution of hydrogen against the constant

* A calorie is the heat necessary to raise 1 g. of water from 15° to 16°C.

pressure of the atmosphere, $-w_p$, is equal to the product of the pressure by the volume of 1 g. of hydrogen, or

$$-w_p = P\Delta V. \tag{2}$$

As 1 g. of hydrogen is evolved, 11.9 l. of hydrogen act against the atmospheric pressure of one atmosphere at room temperature, and since 24.23 cal. are contained in each liter-atmosphere $P\Delta V$ is equal roughly to 290 cal. (the figure used by Gibbs). The total work done *on* the system is equal, therefore, to $w_e + w_p$ or $-290 + (-9{,}256)$ or $-9{,}546$ cal.

To calculate the change in internal energy of the cell we have yet to evaluate the quantity q. The cell must have absorbed 1,288 cal. of heat since the cell plus resistance evolved only 7,968 cal. while the resistance alone was evolving 9,256 cal. Since q is equal to $+1{,}288$ cal. and w to $-9{,}546$ cal., the change in energy of the cell ΔU must be equal to $-8{,}258$ cal., since

$$\Delta U = q + w. \tag{XV-2}$$

This calculation demonstrates the interesting fact that cell (A) when operating under conditions of constant pressure and temperature, is able to do more work than it decreases in energy. In other cells, however, it frequently happens that the decrease in energy is greater than the work done by the cell.

The free-energy increase of the cell ΔG during the reaction is a measure of the increase in energy available for useful work, or conversely the decrease in free energy of the cell, $-\Delta G$, is a measure of the useful work which can be obtained from the cell reaction. In Favre's cadmium hydrogen cell the electrical work w_e is equal to the free-energy decrease, $-\Delta G$, since the work done by the evolution of hydrogen against the constant pressure of the atmosphere is not useful work. We have the important equation, then [compare Eq. (1)]

$$\Delta G = -nFE. \tag{3}$$

Other thermodynamic quantities may be calculated from Favre's data. Equation (XV-10) defines the heat content H by the equation

$$H = U + PV. \tag{XV-10}$$

For the reaction of cell (A) we may write

$$\Delta H = \Delta U + P\Delta V.$$

Since ΔU is equal to $-8{,}258$ cal. and $P\Delta V$ equal to 290 cal., ΔH is equal to $-7{,}968$ cal. This is exactly the value that Favre found for the heat absorbed in the cell and resistance when the whole apparatus was placed in his calorimeter. In general we can say that ΔH is the heat absorbed in a reaction when the reaction is carried out at constant pressure and no work other than PV work is done. In thermochemistry one usually measures ΔH and not ΔU. (It might be pointed out that in the reactions in which no gas is evolved, ΔV is so small that $P\Delta V$ may be neglected in comparison with ΔU, in which case ΔH and ΔU are identical.) In Table I are collected together the various thermodynamic quantities which have been calculated above.*

TABLE I

	Cal.
$\Delta U =$	$-8{,}258$
$\Delta H =$	$-7{,}968$
$q =$	$1{,}288$
$w_e =$	$-9{,}256$
$w_p =$	$-\ \ 290$
$w =$	$-9{,}546$
$\Delta G =$	$-9{,}256$

The concept of free energy is important not only in finding the available work which may be obtained in a chemical reaction, but also in telling us the "affinity" of a reaction. If the free-energy change in a reaction at constant temperature and pressure is zero, the reaction is in equilibrium since one criterion of equilibrium is

$$dT = 0, \qquad dP = 0, \qquad dG = 0. \qquad \text{(XV-23)}$$

If ΔG is negative, work can be done by a reaction and the reaction

* It should be noted that H is a quantity characteristic of the state of the system and that ΔH is the difference in H between two states of the system. Values of ΔH are independent of the method by which the system is changed from the first to the second state. This is not true for the quantity q which may take on all values from zero to ΔU, $-w$, or ΔH, depending on the manner in carrying out the reaction. In the isothermal expansion of a perfect gas, ΔU is zero and $q = -w$. If the expansion occurs at constant pressure, $q = \Delta H = -w$. If the expansion is adiabatic, q is zero. The heat absorbed in a chemical reaction which occurs at constant volume is q, and this is equal to ΔU since no work is done. If the heat of reaction is measured under conditions of constant pressure, q is equal to ΔH.

may proceed spontaneously. If ΔG is positive, the reaction cannot of itself occur. As an example of these statements, we can consider the gaseous reaction

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 \rightarrow HCl; \qquad \Delta G_{298^\circ} = -22{,}692 \text{ cal.}$$

at 298°K. and at atmospheric pressure. The combination of the two elements is accompanied by a large decrease in the free energy; hence the system hydrogen and chlorine gas is very unstable. Hydrogen and chlorine have a great affinity for each other. If the free-energy change is positive, then we know that the reaction cannot of itself occur.* The decomposition of hydrogen chloride may be written

$$HCl \rightarrow \tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2;$$
$$\Delta G_{298^\circ} = 22{,}692 \text{ cal.}$$

Since the free energy increases by a large amount as the reaction runs as written, it is evident that hydrogen chloride is stable at 298°K. and will not decompose spontaneously.

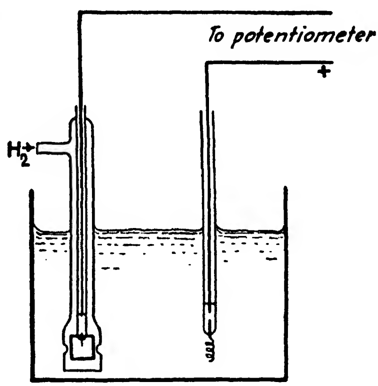


FIG. 1.

In Chap. XIV the hydrogen and silver chloride electrodes were described. Imagine these two electrodes immersed in an $0.1m$† hydrochloric acid solution as pictured in Fig. 1. As the current flows, the hydrogen displaces the silver from the silver chloride, the reaction being

$$\tfrac{1}{2}H_2(1 \text{ atm.}) + AgCl = Ag + HCl(0.1m)$$

and the measured e.m.f. of the cell

$$\text{Pt, } H_2 \mid HCl(0.1m) \mid AgCl \mid Ag \qquad (B)$$

is 0.3522 v.

* See LEWIS and RANDALL, "Thermodynamics," p. 503, McGraw-Hill Book Company Inc., New York, 1923.

† NOYES and ELLIS, *J. Am. Chem. Soc.*, **39**, 2532 (1917). The hydrochloric acid concentration is expressed in this particular instance in moles per 1,000 g. of water (designated by the symbol m).

The change in free energy is, therefore,

$$\Delta G = -nFE = -(0.3522)(96{,}500) \text{ joules}$$

or $-8{,}123$ cal.

The Gibbs and Helmholtz Equation.—Not only is it possible to calculate the free energy of chemical reactions from e.m.f. measurements, but it is also possible to calculate the heat-content change of a reaction ΔH by making e.m.f. measurements of a cell over a range of temperatures at constant pressure. Free energy and heat content are connected by the relation known as the equation of Gibbs and Helmholtz,

$$\Delta G - \Delta H = T\left(\frac{d\Delta G}{dT}\right)_P. \qquad \text{(XV-20)}$$

Since $\Delta G = -nFE$, we may write Eq. (XV-20),

$$\Delta E + \frac{\Delta H}{nF} = T\left(\frac{dE}{dT}\right)_P. \qquad (4)$$

Equation (4) is applicable only to reversible e.m.f. measurements. A test of Eq. (4) can be made by comparing the values of ΔH as calculated from the e.m.f. measurements by means of Eq. (4) with the values of ΔH as determined experimentally by thermochemical methods. Table II includes data taken from a review by Harned* which illustrate the applicability of Gibbs's equation.

TABLE II.—A TEST OF THE GIBBS AND HELMHOLTZ EQUATION (ΔH IN CALORIES)

Cell reaction	E	$-dE/dT \times 10^4$	$-\Delta H$ e.m.f.	$-\Delta H$ thermochem.
(1) $Zn + 2AgCl = ZnCl_2(0.555m) + 2Ag$(0°C.)	1.015	4.02	51,989	52,046
(2) $Pb + 2AgI = PbI_2 + 2Ag$ (25°C.)	0.21069	1.38	11,610	11,650
(3) $Cd + 2AgCl + 2.5H_2O = CdCl_2 \cdot 2.5H_2O + 2Ag$(25°C.)	0.67531	6.5	40,030	39,530
(4) $Cd + PbCl_2 + 2.5H_2O = CdCl_2 \cdot 2.5H_2O + Pb$(25°C.)	0.18801	4.8	15,250	14,650

* H. S. TAYLOR, "A Treatise on Physical Chemistry," Chap. XII, by H. S. Harned, D. Van Nostrand Company, New York, 1931.

It must be pointed out that the temperature coefficient of the e.m.f. has to be determined very accurately in order to calculate ΔH with precision since an error of 0.01 mv. in the measured e.m.f. is equal to an error of approximately 100 cal. in the value of ΔH. Furthermore, it is necessary to know that the cell reaction is really the reaction imagined; one must make sure that the e.m.f. does not measure the free-energy decrease of any other reaction.

The Concentration Cell without Liquid Junction.—The e.m.f. of a galvanic cell is considerably altered by a change in the concentration of the electrolyte of the cell. Ellis* measured the change in potential of the cell

$$\text{Pt, } H_2 \mid HCl(m) \mid Hg_2Cl_2 \mid Hg \qquad (C)$$

as the concentration of the hydrochloric acid is changed and obtained the results of Table III.

TABLE III.—E.M.F. VALUES OF CELL (*C*)

m	*E* at 25°C.
4.484	0.15506
1.9287	0.23589
1.0381	0.27802
0.77137	0.29571
0.50948	0.31865
0.33757	0.33836
0.10040	0.39884
0.03332	0.45258

Ellis's cell is illustrated in Fig. 2 and is merely a combination of the hydrogen and calomel electrodes which have already been described in Chap. XIV. The reaction in the cell as the positive current flows inside the cell from the platinum electrode to the calomel electrode is

$$H_2(1 \text{ atm.}) + Hg_2Cl_2 = 2Hg + 2HCl.$$

The calomel electrode is the positive electrode and the hydrogen electrode the negative electrode as measured by the potentiometer.

A concentration cell without liquid junction may be built by combining two of the Ellis cells (*C*) in such a manner that the net e.m.f. represents the differences of e.m.f. between two different

* J. H. ELLIS, *J. Am. Chem. Soc.*, **38**, 737 (1916).

cells containing HCl at two different concentrations. The resulting cell is written

$$Hg|Hg_2Cl_2|0.1m\ HCl|H_2,\ Pt-Pt,\ H_2|0.01m\ HCl|Hg_2Cl_2|Hg. \quad (D)$$

Cell (*D*) is a concentration cell without a liquid junction; the calomel electrode at the left is the negative electrode and the calomel electrode at the right is the positive electrode. Posi-

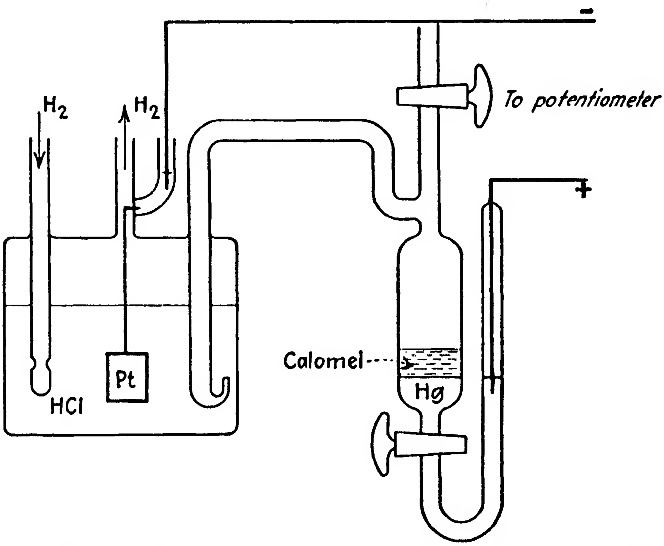


FIG. 2.—Cell for measuring the e.m.f. of the hydrogen-calomel-electrode combination with hydrochloric acid as the electrolyte.

tive electricity inside the cell flows from left to right (as one reads), and the e.m.f. of the whole combination is positive.

We must now consider the reason for the change of e.m.f. with change of concentration (Table III), why a cell similar to (*D*) gives a net e.m.f. Every source of electrical energy, at least in a galvanic cell, must arise from a chemical reaction in the cell as the current flows; hence the e.m.f. of (*D*) must be due to a chemical reaction. In order to discover the chemical reaction which supplies the electrical energy of (*D*), we need only to allow the current to flow; in so doing it is observed that the net effect is the transfer of some hydrogen chloride from the more concentrated solution to the more dilute. Since positive electricity flows inside the cell from left to right, it is evident that at the

calomel electrode to the left chloride ions leave the solution forming calomel, and at the neighboring hydrogen electrode hydrogen ions leave the solution forming hydrogen gas, so that there is a net loss of hydrogen chloride in this half of the concentration cell. At the hydrogen electrode to the right hydrogen ions enter the solution and at the calomel electrode to the right chloride ions enter the solution, so that there is a net gain of hydrogen chloride in this half of the concentration cell. The cell reaction is written

$$\mathrm{HCl}(0.1m) \rightarrow \mathrm{HCl}(0.01m),$$

and the e.m.f. is due to the tendency of hydrochloric acid to diffuse from the more concentrated to the more dilute solution. If the hydrochloric acid is allowed to diffuse by short-circuiting the two calomel electrodes until equilibrium is reached (*i.e.*, concentration of acid the same in both cells), the e.m.f. falls to zero (at equilibrium dG and therefore dE must be zero).

It is a simple matter to calculate the free energy of the reaction of cell (D); since the reaction is a transfer of hydrogen chloride, the free energy is called the free energy of transfer and is obtained most easily from e.m.f. measurements. As before, the free-energy change is equal to the negative of the e.m.f. multiplied by the number of coulombs of electricity passed through the cell. The free energy of transfer can be obtained by measurements of the e.m.f. of cells of type (C) by taking e.m.f. differences between the selected concentrations. For example, the free energy of transfer of one mole of hydrogen chloride from a concentration of 4.484 to a concentration of 1.0381 can be obtained from the data of Table III by subtracting from the e.m.f. at concentration 1.0381 the value of the e.m.f. at the concentration 4.484 and then by substituting the resulting e.m.f., 0.12296, into Eq. (3). The reason the e.m.fs. are subtracted in this way can be understood if the e.m.fs. of the two parts of cell (D) are added together. First assume that the concentrations of cell (D) are 4.484 and 1.0381 instead of 0.1 and 0.01 M; then the e.m.f. of the more concentrated cell is -0.15506 (Table III) and the e.m.f. of the more dilute is $+0.27802$; the sum of the two is 0.12296 v. The e.m.f. of the concentrated cell is taken as negative since the positions of the hydrogen and calomel electrodes are reversed from the positions they have in cell (C) where

the e.m.f. is positive. The free energy of transfer is $-(0.12296)(96{,}500)$ joules or $-2{,}822$ cal. This means that the system as a whole decreases in free energy to the extent of 2,822 cal. as one mole of hydrogen chloride is reversibly and isothermally transferred from the more concentrated to the more dilute solution. It is important to emphasize the fact that as the hydrogen chloride is removed from the more concentrated solution, the concentration of the solution should not change. This can only be true if we have an infinite volume of concentrated solution in the cell. Furthermore as the hydrogen chloride is added to the dilute solution, the concentration of this solution should not change; hence we should have an infinite volume of dilute solution in the cell if we wish to carry out an actual transfer of hydrogen chloride. Although the condition of infinite volume of solution is impossible to satisfy experimentally, nevertheless by measuring the e.m.f. by the Poggendorf balancing method, we find the free energy of transfer of the hydrochloric acid under the theoretical conditions since only an infinitesimal (or nearly infinitesimal) quantity of hydrogen chloride is transferred during the measurement. In this way we can calculate the free energy of transfer of a mole of hydrogen chloride from an infinite volume of concentrated solution to an infinite volume of dilute solution. The free energy of transfer is negative, and the work done by the system is therefore positive.

By measuring the e.m.f. of a concentration cell over a series of temperatures, it is possible to calculate the heat of transfer by the Gibbs equation just as it is possible to calculate the heat of reaction. A simpler method is to calculate ΔH, the change in heat content (the heat of the reaction) at each concentration by the Gibbs equation and then by subtracting the value at one concentration from the ΔH of a second concentration, the change in heat content due to the transfer of the hydrochloric acid is obtained. Ellis* has calculated ΔH at the hydrochloric acid concentration of 4.484 to be $-12{,}240$ cal. and at 1.0381 to be $-15{,}366$ cal. These values are the increase in heat content as one mole of hydrogen chloride is added to the two solutions, respectively. If a mole of hydrogen chloride is removed from the more concentrated solution, the system gains $+12{,}240$ cal. and

* J. H. Ellis, *loc. cit.*

as it is added to the dilute solution the system gains $-15{,}366$ cal., the net gain being $-3{,}126$ cal. In other words, the transfer of one mole of hydrogen chloride from an infinite volume of the concentrated solution to an infinite volume of the dilute solution is accompanied by an evolution of 3,126 cal., the conditions of the experiment being, of course, constant temperature and pressure and the performance of no work except the work done by the expansion of the system against the atmosphere.

The heat evolved in the transfer of the hydrogen chloride between these two solutions is not equal to the heat liberated when a mole of hydrochloric acid at a concentration of 4.484 is diluted with water until the concentration becomes 1.0381 (the usual procedure in thermochemistry) because the process in the two cases is physically different. The transfer of the acid deals with infinite volumes of solution while the dilution of the acid deals with finite volumes.

Concentration cells without liquid junctions can be composed of one electrolyte and two amalgam electrodes such as cell (*E*).

$$\text{Tl amalg. (conc.)} \mid Tl_2SO_4 \text{ solution} \mid \text{Tl amalg. (dil.)}. \qquad (E)^*$$

The e.m.f. of cell (*E*) arises from a difference of concentration of the thallium in the two amalgams, and the e.m.f. is independent of the concentration of the electrolyte. The thallium in the concentrated amalgam has a greater chemical potential and will tend to transfer itself to the dilute amalgam; this can happen by the thallium entering the solution at the left and entering the dilute amalgam at the right; the sign of the left hand electrode is, therefore, negative. All the thermodynamic quantities which we have calculated from the measurements on cell (*D*) can be calculated from the e.m.f. values of (*E*) in exactly the same manner.

E.M.F. and Concentration.—A relation between e.m.f. and concentration may be found by considering the ideal Eq. (XV-56)

$$\mu_i = \mu_i^\circ + RT \ln N_i \qquad \text{(XV-56)}$$

which states that the chemical potential of a component of a phase is a linear function of the logarithm of its mole fraction.

* T. W. Richards and F. Daniels, *J. Am. Chem. Soc.*, **41**, 1732 (1919). For sodium amalgams see Bent and Gilfillan, *ibid.*, **55**, 3989 (1933); **56**, 1505 (1934).

It will be remembered that the chemical potential may be defined in terms of the free energy, *i.e.*,

$$\mu_i = \left(\frac{dG}{dn_i}\right)_{P,T,n_j}. \qquad \text{(XV-38)}$$

The chemical potential of a component is equal to the increase in the free energy of the system when one mole of the component is added to an infinite volume of the phase. The temperature, pressure, and number of other components must remain constant. The difference in chemical potential of a component between two different concentrations may be calculated from e.m.f. values of cell (D) since these values are an exact measure of the difference in the change of free energy of the system when one mole of hydrogen chloride is added to the two solutions having a different concentration. In calculating $\left(\frac{dG}{dn_i}\right)$ from Eq. (3) the number of faradays must be equal to the number of faradays necessary to transfer one mole of substance. For the difference in chemical potential of the hydrogen ion between two concentrations we can write

$$\mu''_{\mathrm{H}^+} - \mu'_{\mathrm{H}^+} = \left(\frac{dG_{\mathrm{H}^+}}{dn_{\mathrm{H}^+}}\right)''_{P,T} - \left(\frac{dG_{\mathrm{H}^+}}{dn_{\mathrm{H}^+}}\right)'_{P,T} \qquad (5a)$$

and for the chloride ion,

$$\mu''_{\mathrm{Cl}^-} - \mu'_{\mathrm{Cl}^-} = \left(\frac{dG_{\mathrm{Cl}^-}}{dn_{\mathrm{Cl}^-}}\right)''_{P,T} - \left(\frac{dG_{\mathrm{Cl}^-}}{dn_{\mathrm{Cl}^-}}\right)'_{P,T}, \qquad (5b)$$

Adding (5a) and (5b), we obtain

$$\mu''_{\mathrm{HCl}} - \mu'_{\mathrm{HCl}} = \left(\frac{dG_{\mathrm{HCl}}}{dn_{\mathrm{HCl}}}\right)''_{P,T} - \left(\frac{dG_{\mathrm{HCl}}}{dn_{\mathrm{HCl}}}\right)'_{P,T}. \qquad (6)$$

After substitution of the e.m.f. in Eq. (6) we have

$$\mu''_{\mathrm{HCl}} - \mu'_{\mathrm{HCl}} = nF(E' - E''), \qquad (7)$$

where n is the number of faradays necessary to transfer one mole of the hydrogen chloride between the two concentrations.*

* A more detailed derivation of Eq. (7) may help to make clear the reasoning involved in passing from Eq. (6) to Eq. (7). Let us consider, for

Equation (XV-56) as applied to the hydrogen ion may be written

$$\mu_{H^+} = \mu^{\circ}_{H^+} + RT \ln N_{H^+}, \tag{8a}$$

and for the chloride ion

$$\mu_{Cl^-} = \mu^{\circ}_{Cl^-} + RT \ln N_{Cl^-}. \tag{8b}$$

Adding Eqs. (8*a*) and (8*b*),

$$\mu_{HCl} = \mu^{\circ}_{HCl} + RT \ln N_{H^+} \cdot N_{Cl^-}. \tag{9}$$

Combining Eqs. (9) and (7) an expression for the e.m.f. in terms of the mole fraction results:

$$nF(E' - E'') = RT \ln \frac{N''_{H^+}\, N''_{Cl^-}}{N'_{H^+}\, N'_{Cl^-}}. \tag{10}$$

Equation (10) is valid only for those solutions for which equation (XV-56) is also valid, *i.e.*, ideal solutions of a given solvent. In

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example, the cell

$$\text{Pt, H}_2 \left| \begin{matrix}\text{HCl}\\ m'\end{matrix} \right| \text{AgCl} \,\Big|\, \text{Ag}. \tag{F}$$

When the electrical current is allowed to flow through cell (*F*), the following reaction occurs:

$$\tfrac{1}{2}H_2 + AgCl \rightarrow H^+ + Cl^- + Ag. \tag{7a}$$

The net change in chemical potential $\Delta\mu$ is equal to the sum of the chemical potentials of the products minus the chemical potentials of the reactants, or

$$\Delta\mu' = \mu'_{Ag} + \mu'_{H^+} + \mu'_{Cl^-} - \tfrac{1}{2}\mu'_{H_2} - \mu'_{AgCl}. \tag{7b}$$

The e.m.f. of the cell (*F*) is given in terms of $\Delta\mu$ by the equation

$$\Delta\mu' = -nFE', \tag{7c}$$

where n is the number of faradays necessary to carry out the reaction as written in Eq. (7*a*). If the concentration of the acid in cell (*F*) is at some other concentration, say m'', we can write

$$\Delta\mu'' = \mu''_{Ag} + \mu''_{H^+} + \mu''_{Cl^-} - \tfrac{1}{2}\mu''_{H_2} - \mu''_{AgCl} \tag{7d}$$

and

$$\Delta\mu'' = -nFE''. \tag{7e}$$

Let us now form a concentration cell of cell (*F*) obtaining the cell (*G*)

$$\text{Pt, H}_2 \left| \begin{matrix}\text{HCl}\\ m'\end{matrix} \right| \text{AgCl} \,\Big|\, \text{Ag} - \text{Ag} \,\Big|\, \text{AgCl} \left| \begin{matrix}\text{HCl}\\ m''\end{matrix} \right| \text{H}_2\text{, Pt}. \tag{G}$$

As the current flows the following reaction occurs,

order to test the applicability of Eq. (10) let us consider the accurate values for the e.m.f. of the cell

$$\text{Pt, } H_2 \,|\, HCl(m) \,|\, AgCl \,|\, Ag \tag{F}$$

at 25°C. which have recently been determined experimentally by Carmody.* First let us transform cell (F) into a concentration cell without liquid junction, *viz.*,

$$\text{Pt, } H_2 \left| \begin{matrix} HCl \\ \textit{dil.} \end{matrix} \right| AgCl \,\Big|\, Ag - Ag \,\Big|\, AgCl \left| \begin{matrix} HCl \\ \textit{concn.} \end{matrix} \right| H_2\text{, Pt.} \tag{G}$$

The e.m.f. of cell (G) in terms of the e.m.fs. of cell (F) is the sum of the e.m.fs. of the dilute cell and of the concentrated cell or

$$E = E_{dil.} - E_{concn.} = \frac{RT}{nF} \ln \frac{N_{H^+} \cdot N_{Cl^-\,(concn.)}}{N_{H^+} \cdot N_{Cl^-\,(dil.)}}. \tag{11}$$

The e.m.f. of the concentrated cell is negative since its electrodes are reversed in comparison with cell (F). If we call the e.m.f. of cell (F) positive, and that is our convention, then the e.m.f. of

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$$HCl(m'') \rightarrow HCl(m') \tag{7f}$$

and the net change in chemical potential is

$$\mu'_{HCl} - \mu''_{HCl} = \Delta\mu_{HCl}. \tag{7g}$$

Furthermore

$$\Delta\mu_{HCl} = -nFE, \tag{7h}$$

where E is the e.m.f. of cell (G). To show the relation between Eq. (7g) and the e.m.f., let us subtract (7d) from (7b), obtaining

$$\Delta\mu' - \Delta\mu'' = \mu_{H^+} + \mu'_{Cl^-} - \mu''_{H^+} - \mu''_{Cl} \tag{7i}$$

or

$$\Delta\mu' - \Delta\mu'' = \mu'_{HCl} - \mu''_{HCl},$$

since the chemical potential of hydrochloric acid is equal to the sum of the chemical potentials of its ions and since the chemical potentials of silver, silver chloride and hydrogen gas are the same in the two cells. Introducing the e.m.f. by means of Eqs. (7c) and (7e), we have

$$-nFE' + nFE'' = \mu'_{HCl} - \mu''_{HCl}$$

or

$$\mu''_{HCl} - \mu'_{HCl} = nF(E' - E''),$$

which is Eq. (7).

* W. R. Carmody, *J. Am. Chem. Soc.*, **54**, 188 (1932); see also Harned and Ehlers, *ibid.*, **54**, 1350 (1932).

the concentrated half of cell (G) must be negative since the cell arrangement is reversed.

Before we can apply Eq. (11) there is still one more transformation which we must make. Carmody did not express his concentration in terms of mole fraction, but in terms of moles per 1,000 grams of water. Let us symbolize this concentration unit by the letter m, then we can write Eq. (11)

$$E = E_{dil.} - E_{concn.} = \frac{2RT}{nF} \ln \frac{m_{\mathrm{HCl}\ (concn.)}}{m_{\mathrm{HCl}\ (dil.)}}, \tag{12}$$

since $m_{\mathrm{H}^+} = m_{\mathrm{Cl}^-} = m_{\mathrm{HCl}}$. This substitution of m''/m' for N''/N' is valid for dilute solutions only (solutions in which the number of moles of salt is small in comparison to the number of moles of water).* Carmody's data are given in Table IV in which the first column gives the concentration, the second column the e.m.f. of cell (F), the third column the e.m.f. of cell (G), the fourth column values of cell (G) calculated by means of Eq. (12) and the last column the difference between the calculated and observed values. In this calculation the dilute solution of cell (G) is held constant at $0.0003288m$ and the concentration of the concentrated half of cell (G) is varied.

The data of Table IV are all at 25°C. and the value of $2\,RT/nF$ ln is taken to be 0.1183 log, (ln is the symbol for natural logarithms, Napierian logarithms, and log is the symbol for logarithms to the base 10, Briggsian logarithms).

* The mole fraction of a substance is defined for a solution composed of solvent and single solute by the equation

$$N_i = \frac{n_i}{n_s + (\nu_+ + \nu_-)n_i},$$

where n_i is the number of moles of an ionizing solute, n_s is the number of moles of solvent, and ν is the number of ions of one kind that one molecule of solute dissociates into. Since the concentration unit, moles per 1,000 g. of solvent, is defined by the equation

$$m_i = \frac{n_i}{0.001w_s n_s},$$

where w_s is the molecular weight of the solvent, it is evident that

$$\log N_i = \log m_i - \log\,(1 + 0.001(\nu_+ + \nu_-)mw_s) + \log 0.001w_s.$$

The calculations show that the ideal Eq. (12) predicts e.m.f. values to which the observed data approach closer and closer as the concentration gets more dilute.

TABLE IV

m	$E_{(F)}$	$E_{(G)}$	$E_{(G)\,\text{calcd.}}$	Diff.
0.1165	0.3449	0.2904	0.3018	0.0114
0.1083	0.3483	0.2870	0.2980	0.0110
0.1056	0.3496	0.2857	0.2968	0.0111
0.09425	0.3552	0.2801	0.2908	0.0107
0.04572	0.3901	0.2452	0.2536	0.0084
0.009582	0.4660	0.1693	0.1734	0.0041
0.004965	0.4987	0.1366	0.1396	0.0030
0.002799	0.5271	0.1082	0.1102	0.0020
0.001910	0.5462	0.0891	0.0906	0.0015
0.001129	0.5727	0.0626	0.0636	0.0010
0.0007280	0.5950	0.0403	0.0410	0.0007
0.0005518	0.6090	0.0263	0.0268	0.0005
0.0003288	0.6353			

The activity coefficient, the function invented by G. N. Lewis and defined by Eq. (XV-57) is exceedingly useful as a measure of the departure of solutions from ideality. The activity coefficient of the solute has the great advantage of going to unity when the concentration becomes zero. The chemical potential, on the other hand, is equal to minus infinity at zero concentration. Introducing the activity coefficient into Eq. (11), we obtain the equation,

$$E = E_{dil.} - E_{concn.} = \frac{RT}{nF}\ln\left[\frac{N_{H^+}\cdot N_{Cl^-}\cdot f_{H^+}\cdot f_{Cl^-\,(concn.)}}{N_{H^+}\cdot N_{Cl^-}\cdot f_{H^+}\cdot f_{Cl^-\,(dil.)}}\right]. \tag{13}$$

Since the activity coefficient of an ion has no physical significance, as will be shown in a later chapter, it is customary not to deal with the ionic activity coefficients but with the so-called "mean activity coefficient," $f_\pm$, defined by the equation,

$$(f_\pm)^{\nu_+ + \nu_-} = (f_+)^{\nu_+}\cdot(f_-)^{\nu_-}, \tag{14}$$

where ν is the number of ions of one kind that a molecule of the solute dissociates into. For hydrochloric acid,

$$f_{\pm\text{HCl}} = \sqrt{f_{H^+}\cdot f_{Cl^-}} \tag{15a}$$

and for barium chloride, for example,

$$(f_{\pm})^3 = f_{Ba^{++}} \cdot f^2_{Cl^-}$$

or

$$f_{\pm BaCl_2} = \sqrt[3]{f_{Ba^{++}} \cdot f^2_{Cl^-}}. \tag{15b}$$

The activity coefficient denoted by the symbol f is defined in terms of the mole fraction, Eq. (XV-57); in the case of Eq. (12) which relates the e.m.f. to the concentration in units of moles per 1,000 grams of water let us introduce an activity coefficient defined in terms of this concentration unit and denoted by the symbol γ, a symbol used by Lewis and Randall. Equation (12) becomes, then,

$$E = E_{dil.} - E_{concn.} = \frac{RT}{F} \ln \frac{m_{H^+} \cdot m_{Cl^-} \cdot \gamma_{H^+} \cdot \gamma_{Cl^-\,(concn.)}}{m_{H^+} \cdot m_{Cl^-} \cdot \gamma_{H^+} \cdot \gamma_{Cl^-\,(dil.)}},$$

or

$$E = E_{dil.} - E_{concn.} = 2\frac{RT}{F} \ln \frac{m_{HCl} \cdot \gamma_{\pm HCl\,(concn.)}}{m_{HCl} \cdot \gamma_{\pm HCl\,(dil.)}}. \tag{16a}$$

For barium chloride, for example, the analogous equation would be

$$E = E_{dil.} - E_{concn.} = \frac{3}{2}\frac{RT}{F} \ln \frac{m_{BaCl_2} \cdot \gamma_{\pm BaCl_2\,(concn.)}}{m_{BaCl_2} \cdot \gamma_{\pm BaCl_2\,(dil)}}. \tag{16b}$$

In the case of barium chloride two faradays of electricity must flow through the cell in order to transfer one mole of barium chloride, hence the factor 2 in the denominator of equation (16*b*).*

* It is important to understand the significance of the definitions of γ and of f. Since the activity coefficient f is defined by the equation

$$\mu_i = \mu_i^\circ + RT \ln N_if_i \tag{17a}$$

and since the activity coefficient γ might be defined by the equation

$$\mu_i = \mu_i^\circ + RT \ln m_i\gamma_i, \tag{17b}$$

it might be supposed that

$$N_if_i = m_i\gamma_i, \tag{17c}$$

but this is not true because γ and f are defined by convention to equal unity at zero concentration which means that at this concentration they must be equal to each other. But by Eq. (17*c*) f_i and γ_i could not be equal to each other unless N_i equals m_i and this is not true (see footnote, p. 257). The relation between $f_{\pm}$ and $\gamma_{\pm}$ is given by the equation

$$\log f_{\pm} = \log \gamma_{\pm} + \log [1 + 0.001(\nu_+ + \nu_-)mw_s]. \tag{17d}$$

If equation (17*c*) were true, the relationship would be

Let us now calculate the mean activity coefficient of hydrochloric acid at each value of the concentration of Table IV. In order to do this equation, Eq. (16a) must be rearranged so that we can extrapolate to zero concentration where the activity coefficient is by definition equal to unity. At some particular value of the concentration the term $m_{\text{HCl}} \cdot \gamma_{\pm\text{HCl}}$ will be equal to unity and so disappear from Eq. (16a). Let us designate by $E°$ the value of cell (F) when $m_{\text{HCl}} \cdot \gamma_{\pm\text{HCl}}$ is equal to unity. Making this convention Eq. (16a) becomes

$$E_{dil.} - E° = 2\frac{RT}{F} \ln \frac{1}{m_{\text{HCl}}\gamma_{\pm\text{HCl}(dil.)}}$$

or

$$E = E° - 2\frac{RT}{F} \ln m_{\text{HCl}} \cdot \gamma_{\pm\text{HCl}}. \tag{18}$$

Equation (18) may also be written (at 25°C.)

$$E + 0.1183 \log m_{\text{HCl}} = E° - 0.1183 \log \gamma_{\pm\text{HCl}}. \tag{19}$$

At zero concentration the left-hand side of Eq. (19) must equal $E°$ since γ is unity at zero concentration and the logarithm of unity is zero. We can plot values of $E + 0.1183 \log m$ as some function of the concentration and by extrapolating to zero concentration obtain $E°$. When we once know $E°$, the calculation of $\gamma_{\pm\text{HCl}}$ for any concentration at which E is known can be carried out by means of Eq. (19). Carmody's calculations are given in

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$$\log f_{\pm} = \log \gamma_{\pm} + \log \{1 + 0.001(\nu_+ + \nu_-)mw_s\} - \log 0.001w_s. \tag{17e}$$

From the definition of γ given by (17b) or (17e) it is evident that $f_{\pm}$ and $\gamma_{\pm}$ would not be equal to each other and to unity at zero concentration; but by accepting (17d) as the definition of γ, the convention of unit values of f and γ at infinite dilution is fulfilled. We define, therefore, f_i by Eq. (17a) and γ by Eq. (17d). The $E°$ values given below are the values of the e.m.f. of the cell under consideration when $m\gamma$ equals unity; this e.m.f., $E°$, will not be equal to the e.m.f. of the cell when Nf is equal to unity, but the latter e.m.f. may be found by adding $\frac{(\nu_+ + \nu_-)RT}{nF} \ln 0.001w_s$ to $E°$.

A general equation for the e.m.f. of a concentration cell without liquid junction is

$$\Delta E = E_{dil.} - E_{concn.} = \frac{(\nu_+ + \nu_-)}{(z_i\nu_i)} \frac{RT}{F} \ln \frac{m \cdot \gamma_{\pm(concn.)}}{m \cdot \gamma_{\pm(dil.)}}. \tag{17f}$$

Table V and values of $E + 0.1183 \cdot \log m_{HCl}$ are plotted as a function of the square root of the concentration in Fig. 3. The reason for plotting the data against the square root of the concentration will be shown theoretically in the next chapter. Practically, this method of plotting has the advantage of yielding a straight line which makes extrapolation to zero concentration more reliable. The extrapolated value at $E°$ is 0.2223 v.

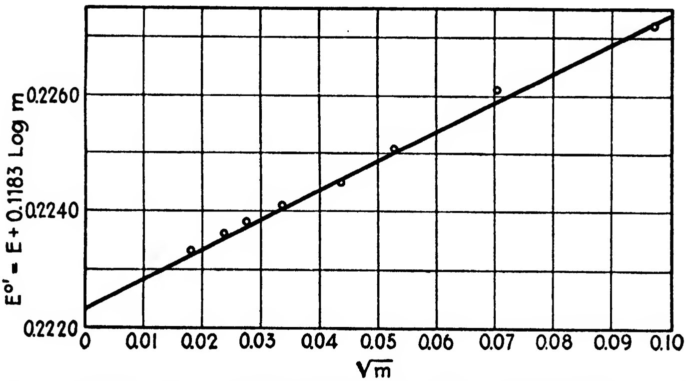

FIG. 3.—Values of (E + 0.1183 log m) as a function of the square root of the concentration.

From Table V it is evident that, as the concentration increases, the activity coefficient falls off; the solutions deviate more and more from the behavior of a perfect solution. But before dis-

TABLE V.—E.M.F. DATA IN VOLTS AND MEAN ACTIVITY COEFFICIENTS FOR HYDROCHLORIC ACID AT 25°C.

m	E	$E + 0.1183 \log m$	$\gamma_{\pm}$
0.1056	0.3496	0.2341	0.794
0.09425	0.3552	0.2338	0.800
0.04572	0.3901	0.2316	0.836
0.009582	0.4660	0.2272	0.909
0.004965	0.4987	0.2261	0.929
0.002799	0.5271	0.2251	0.948
0.001910	0.5462	0.2245	0.959
0.001129	0.5727	0.2241	0.966
0.0007280	0.5950	0.2238	0.971
0.0005518	0.6090	0.2236	0.975
0.0003288	0.6353	0.2233	0.979

cussing theories which attempt to explain the variation of the activity coefficient with change of concentration, let us see what other purely thermodynamic calculations can be made with the data of e.m.f. cells without liquid junctions.

Standard Electrode Potentials.—Many years ago Volta arranged the metals in order of their effectiveness in producing jerks of the frog's legs. Ever since his time scientists have been measuring and comparing the potentials of different electrodes and there have slowly developed accurate methods for the measurement of electrode potentials and methods for the calculation of these potentials in a significant way. As examples of standard electrode potentials let us consider the standard electrode potentials of the two electrodes of cell (*F*). Any e.m.f. measurement that we can make will always be the sum of at least two potentials (usually three or more); thus in cell (*F*) the total e.m.f. measures the sum of the potentials at the phase boundary Pt, H_2 | HCl, at the phase boundary HCl | AgCl, at the phase boundary AgCl | Ag and at the junction of the metals platinum and silver. In order to calculate the value of any single-phase boundary potential of cell (*F*), or any other single-electrode potential, it is essential that we arbitrarily define the potential at two phase boundaries. The conventions which have been adopted by electrochemists are to assign a value of zero potential to the metal, metal junction, such as the junction between the platinum and silver of cell (*F*),* and to assign a value of zero potential to the potential of the phase boundary Pt, H_2 | H^+ when the cell is at 25°C., the hydrogen gas pressure equal to the standard atmospheric pressure, 760 mm., of Hg at 0°C., and the concentration of the hydrogen ion such that $m_{H^+}\gamma_{H^+}$ is equal to unity. The sign of a standard electrode potential is determined by the sign of the measured e.m.f. when the cell is written down with the hydrogen electrode at the left and the electrode whose standard potential we wish to measure at the right. Thus, the standard electrode potential for the electrode Cl^- | AgCl | Ag is +0.2223 v. at 25°C. since $E°$ for the cell

$$\text{Pt, } H_2 \mid \text{HCl} \mid \text{AgCl} \mid \text{Ag} \qquad (F)$$

* The junction between the platinum and silver is made during the e.m.f. measurement.

is positive as demonstrated above. In other words, the entire standard e.m.f. (E°) of cell (F) is by definition set equal to the standard electrode potential of the silver chloride electrode. The definition of the standard electrode potential for an electrode other than the hydrogen electrode is the value of the e.m.f. of the cell composed of the standard hydrogen electrode and the electrode in question when the electrode is immersed in a solution of its ions of such a concentration that $m_i\gamma_i$ is equal to unity. As an example of the foregoing conventions let us calculate the standard electrode potential of the zinc electrode, $Zn^{++} \mid Zn$. The standard electrode potential of this electrode may be obtained by adding together the E° values of the following cells:*

$$\text{Pt, } H_2 \mid \text{HCl} \mid \text{AgCl} \mid \text{Ag} \qquad E^\circ = +0.2223 \text{ v.} \tag{F}$$

and

$$(+)\text{Ag} \mid \text{AgCl} \mid \text{ZnCl}_2 \mid \text{Zn}(-) \qquad E^\circ = -0.9839 \text{ v.} \tag{H}$$

The result of the addition gives for E° for the $Zn^{++} \mid Zn$ electrode -0.7616 v. Some standard electrode potentials taken from the "International Critical Tables"† are given in Table VI. These potentials are for 25°C. and are based on the moles per 1,000 grams of water-concentration unit. If standard electrode potentials at some other temperature are desired, we make the same conventions as were made above, setting the potential of the electrode Pt, H_2 (1 atm.) $\mid H^+(m_{H^+}\gamma_{H^+} = 1)$ equal to zero at the temperature in question.

It will be observed that the values of the zinc and silver chloride electrodes in Table VI do not agree exactly with the values quoted in the above discussion; this is because the precise value of the last figure of E° for each electrode in the table is experimentally uncertain.

Applications of the Standard Electrode Potential.—The standard electrode potentials are very useful and important in chemistry not only in aiding the chemist to list the elements in the order of their activity or ability to replace other elements, but

* Lewis and Randall, "Thermodynamics," p. 420, McGraw-Hill Book Company, Inc., New York, 1923.

† Vol. VI, p. 332.

also to enable him to calculate equilibrium constants of reactions. From Eq. (XV-64), we have

$$-\Delta G^\circ = -RT \ln K, \qquad \text{(XV-64)}$$

where ΔG° is the free-energy increase of a reaction when the reactants in their standard state react to give the products in their

TABLE VI.—STANDARD ELECTRODE POTENTIALS AT 25°C.

Electrode	Electrode reaction	E°
Li^+, Li	$Li^+ + \epsilon^- = Li$	−2.9595
Rb^+, Rb	$Rb^+ + \epsilon^- = Rb$	−2.9259
K^+, K	$K^+ + \epsilon^- = K$	−2.9241
Ca^{++}, Ca	$Ca^{++} + 2\epsilon^- = Ca$	−2.76
Na^+, Na	$Na^+ + \epsilon^- = Na$	−2.7146
OH^-, H_2	$H_2O + \epsilon^- = \frac{1}{2}H_2 + OH^-$	−0.8295
Zn^{++}, Zn	$Zn^{++} + 2\epsilon^- = Zn$	−0.7618
Fe^{++}, Fe	$Fe^{++} + 2\epsilon^- = Fe$	−0.441
Cd^{++}, Cd	$Cd^{++} + 2\epsilon^- = Cd$	−0.4013
Ni^{++}, Ni	$Ni^{++} + 2\epsilon^- = Ni$	−0.231
Sn^{++}, Sn	$Sn^{++} + 2\epsilon^- = Sn$	−0.136
Pb^{++}, Pb	$Pb^{++} + 2\epsilon^- = Pb$	−0.122
Pt, H_2, H^+	$\frac{1}{2}H_2 = H^+ + \epsilon^-$	0.0000
Br^-, AgBr, Ag	$AgBr + \epsilon^- = Ag + Br^-$	0.0734
Cl^-, AgCl, Ag	$AgCl + \epsilon^- = Ag + Cl^-$	0.2221
Normal calomel electrode	(mole per liter of solution)	0.2805
Decinormal calomel electrode	(decimole per 1000 g. H_2O)	0.3334
Cu^{++}, Cu	$Cu^{++} + 2\epsilon^- = Cu$	0.3441
I^-, $\frac{1}{2}I_2$, Pt	$\frac{1}{2}I_2 + \epsilon^- = I^-$	0.5345
Ag^+, Ag	$Ag^+ + \epsilon^- = Ag$	0.7978
Hg_2^{++}, 2Hg(l)	$Hg_2^{++} + 2\epsilon^- = 2Hg(l)$	0.7986
Br^-, $\frac{1}{2}Br_2(l)$, Pt	$\frac{1}{2}Br_2^-(l) + \epsilon^- = Br^-$	1.0648
Cl^-, $\frac{1}{2}Cl_2$, Pt	$\frac{1}{2}Cl_2^-(g) + \epsilon^- = Cl^-$	1.3583
Au^{+++}, Au	$Au^{+++} + 3\epsilon^- = Au$	1.36

standard state and K is the equilibrium constant of the reaction. Since

$$\Delta G = -nFE, \qquad (3)$$

we can write

$$nFE^\circ = RT \ln K. \qquad (20)$$

But E° is the standard electrode potential or the potential of the metal when immersed in a solution of its ions of such concentration that $m_i\gamma_i$ equals unity. The standard state, therefore, must

be the state where the concentration of a component multiplied by its activity coefficient is equal to unity. Let us consider the reaction which takes place in cell (*F*) when the current is allowed to flow through the cell, or rather let us consider the reaction when it has come to equilibrium. The equilibrium is

$$\tfrac{1}{2}H_2 + AgCl \rightleftarrows H^+ + Cl^- + Ag. \tag{21a}$$

We also have the following equilibrium since the solution is saturated with silver chloride:

$$AgCl \rightleftarrows Ag^+ + Cl^-. \tag{21b}$$

At equilibrium the sum of the chemical potentials of the reactants must equal the sum of the chemical potentials of the products, so we can write

$$\mu_{H^+} + \mu_{Cl^-} + \mu_{Ag} - \tfrac{1}{2}\mu_{H_2} - \mu_{AgCl} = 0$$

from Eq. (21*a*), and

$$\mu_{AgCl} = \mu_{Ag^+} + \mu_{Cl^-}$$

from Eq. (21*b*). Eliminating the chemical potential of the silver chloride, we have

$$\mu_{H^+} + \mu_{Ag} - \tfrac{1}{2}\mu_{H_2} - \mu_{Ag^+} = 0.$$

Replacing the chemical potential by its value as given by Eq. (XV-57) and collecting the constant terms in the manner by which Eq. (XV-62) was derived we obtain the mass action equation

$$K = \frac{(N_{H^+} \cdot f_{H^+})(N_{Ag} \cdot f_{Ag})}{(N_{H_2} \cdot f_{H_2})^{1/2}(N_{Ag^+} \cdot f_{Ag^+})}. \tag{22}$$

For the solid silver of Eq. (22) and for the hydrogen gas when its pressure is equal to 1 atm., we define the activity coefficient so that Nf in each case is equal to unity (both N and f for silver and hydrogen are equal to unity). Making this convention, Eq. (22) becomes

$$K = \frac{N_{H^+} \cdot f_{H^+}}{N_{Ag^+} \cdot f_{Ag^+}}. \tag{23}$$

Eliminating K by means of Eq. (20) and replacing Nf by $m\gamma$

$$\frac{m_{H^+}\gamma_{H^+}}{m_{Ag^+}\gamma_{Ag^+}} = exp\frac{nFE^\circ}{RT} = 1 \times 10^4 \text{ (approximately)} \tag{24}$$

since E° is $+0.2223$ v. Equation (24) states that hydrogen will displace silver ions from solution until the concentration of the hydrogen ions is approximately 10^4 as great as the concentration of the silver ions. Incidentally, it might be pointed out that Eq. (24) demonstrates that whereas individual ionic activity coefficients have no thermodynamic significance, the ratio of activity coefficients of ions of like charge does. It has already been pointed out that the product of the activity coefficients of ions of opposite charge has thermodynamic significance.

As a further example of the applications of standard electrode potentials let us consider the calculation of the ionic product of water. The ionization of water may be represented by the equilibrium

$$H_2O \rightleftarrows H^+ + OH^-.$$

The mass action equation for this equilibrium is

$$K = \frac{N_{H^+} \cdot f_{H^+} \cdot N_{OH^-} \cdot f_{OH^-}}{N_{H_2O} \cdot f_{H_2O}} \tag{25}$$

In pure water, N_{H_2O}, f_{H_2O}, f_{H^+} and f_{OH^-} are all equal to unity (N_{H_2O} is practically unity), so we can write Eq. (25) (valid for pure water only)

$$K = N_{H^+} \cdot N_{OH^-} \qquad \text{or} \qquad K_w = m_{H^+} \cdot m_{OH^-}. \tag{26}$$

From Table VI we find that E° for the reaction

$$H_2O + \epsilon^- = \tfrac{1}{2}H_2 + OH^-$$

is -0.8295. For the reaction

$$\tfrac{1}{2}H_2 = H^+ + \epsilon^-$$

E° is zero. Adding both equations, we have the reaction

$$H_2O = OH^- + H^+,$$

and E° equal to -0.8295. Since

$$K = exp\frac{nFE^\circ}{RT},$$

K_w is equal to $+0.947 \times 10^{-14}$.

By combining standard electrode potentials for different electrodes it is possible to determine the e.m.f., free-energy change,

and equilibrium constants for many reactions in which it is impossible to determine these quantities experimentally or for which direct experimental data are not available.

E.M.F. and Pressure.—In the case of gaseous electrodes such as the hydrogen electrode, the potential of the electrode varies with the pressure of the gas as well as with the concentration of the electrolyte. Assuming that the gas obeys the perfect gas law, that it is diatomic (*i.e.*, two faradays of current flow in transferring one mole of the gas from a cell containing gas at pressure P'' to a cell containing gas at pressure P') and that the volume changes of the solids and solutions are small in comparison with that of the gas, the equation for the change of e.m.f. with change of gas pressure is

$$E = \frac{RT}{2F} \ln \frac{P''}{P'}. \tag{27}$$

Equation (27) is commonly employed for correcting the e.m.f. of cells with hydrogen electrodes to a hydrogen gas pressure of one atmosphere. The cell whose e.m.f. is given by Eq. (27) is

$$\begin{array}{l|c|l} \text{Pt, } H_2 & \text{electrolyte containing hydrogen ions} & H_2\text{, Pt} \\ P_{H_2} = P'' & & P_{H_2} = P' \end{array} \qquad (I)$$

where P'' is a higher pressure than P'. Note that in the case of this cell the electrode at which the pressure of the hydrogen gas is the greatest is written at the left in order that the right-hand electrode may be the positive electrode. Current flows through the cell from left to right since hydrogen gas has a greater tendency to dissolve as hydrogen ions at the left electrode than at the right.

E.M.F. and Valence.—From the equations for the e.m.f. as a function of concentration given above, it is evident that the e.m.f. is inversely proportional to the number of faradays of electricity necessary to transfer one mole of substance in the electrode reaction or, what amounts to the same thing, the e.m.f. is inversely proportional to the valence of the ion formed. If we consider the potential at a single electrode such as mercury immersed in a solution of mercurous nitrate, the change of potential with change of concentration will be only half as great if mercury goes into solution as the ion Hg_2^{++} valence equal to two as if the mercury goes into solution as the ion Hg^+, valence equal to one. Both of

these ions would be called mercurous since the valence of the mercury atom is in each case unity, but the former is a divalent *ion* and the latter a monovalent ion. Ogg* has measured the change of potential at a mercury electrode as the concentration of mercurous nitrate was changed tenfold. Since the observed change in e.m.f. was only half of 0.059 v., the theoretical value assuming an ionic valence of unity, he concluded that the mercurous ion in solution is really Hg_2^{++} and not Hg^+. In a similar way Kasarnowsky† has discovered that the negative telluride ion is $Te_2^=$ rather than Te^-.

Exercises

1. In 1869, Favre carried out the following experiment: He short-circuited a zinc sulfuric acid platinum cell by a resistance and found that the heat evolved by one faraday of electricity flowing through the resistance was 16,950 cal. The cell and resistance placed together in a calorimeter evolved 15,899 cal. Calculate the electrical work, the free-energy increase, the heat-content increase, and the total-energy increase of the system for the reaction

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2.$$

2. Assuming that Favre's experiment was performed reversibly at 25°C., calculate the entropy increase in the reaction of Exercise 1.

3. Prove that $\dfrac{d\frac{\Delta G}{T}}{dT} = \dfrac{-\Delta H}{T^2}$ is an alternative form of the Gibbs and Helmholtz equation.

4. Calculate the equilibrium constant of the reaction $Cu + 2AgNO_3 \rightleftarrows Cu(NO_3)_2 + 2Ag$. What will be the approximate concentration of silver ions in solution if the final copper concentration is 0.01*m*?

5. Derive the correct thermodynamic expression for the e.m.f. of the cells

$$Cd \left| \begin{matrix} CdSO_4 \\ m' \end{matrix} \right| HgSO_4 \left| Hg - Hg \right| HgSO_4 \left| \begin{matrix} CdSO_4 \\ m'' \end{matrix} \right| Cd,$$

$$Hg, Na \left| \begin{matrix} Na_2SO_4 \\ m' \end{matrix} \right| HgSO_4 \left| Hg - Hg \right| HgSO_4 \left| \begin{matrix} Na_2SO_4 \\ m'' \end{matrix} \right| Na, Hg.$$

6. In a chlorine electrode cell in which the e.m.f. arises from a difference in pressure of the chlorine gas, which electrode will be positive and which negative? Write down the cell assuming platinum electrodes.

7. Harned and Fleysher find that the e.m.f. of the cell

$$H_2 \mid (0.1m)\ HCl \text{ in } H_2O \mid AgCl \mid Ag$$

* Ogg, *Z. physik. Chem.*, **27**, 285 (1898).
† Kasarnowsky, *Z. anorg. Chem.*, **128**, 17 (1923).

at 25° is 0.3521 v. and that the e.m.f. of the cell

$$H_2 \mid (0.1m)\ HCl \text{ in } 25 \text{ mole } \%\ C_2H_5OH \text{ and } 75 \text{ mole } \%\ H_2O \mid AgCl \mid Ag$$

at 25°C. is 0.3279.

Calculate the ratio of the activity coefficient of the hydrochloric acid in the alcohol-water mixture to the activity coefficient of the hydrochloric acid in water. (In the second cell the concentration unit is moles per 1,000 g. of mixed solvent.)

8. In Chap. XXV a cell without liquid junction is described which transfers one mole of water per faraday. Calculate the e.m.f. of a "water" concentration cell, one solution in the cell being pure water and the other solution 0.2 N H_2O and 0.8 N alcohol.

CHAPTER XVII

THEORETICAL INTERPRETATION OF THE ACTIVITY COEFFICIENTS OF ELECTROLYTES. I

Variation of Activity Coefficient with Concentration.—In the last chapter an equation relating the e.m.f. to the concentration was described, but as this equation was based on the assumption of an ideal solution, the data did not agree with the equation. As a measure of the extent to which the behavior of an actual solution deviates from the behavior of a perfect solution the activity coefficient was introduced. In Fig. 1 the activity coefficient of hydrochloric acid whose behavior is typical is plotted as a function of the concentration, and it can be seen that at very low concentrations the activity coefficient is nearly unity, but as the concentration increases, the activity coefficient falls off until it reaches a minimum. At higher concentrations it rises even above unity so that at a concentration of $3m$ the activity coefficient is 1.32.

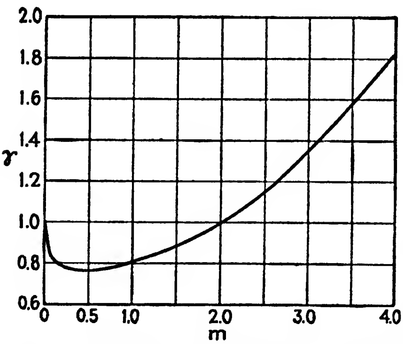

FIG. 1.—Activity coefficient of hydrochloric acid at 25°C.

The activity coefficient of hydrochloric acid is not only a function of its own concentration, but it also depends upon the presence and concentration of other electrolytes. Harned* and his coworkers have been the chief workers in deter-

* H. S. HARNED, *J. Am. Chem. Soc.*, **38,** 1986 (1916); **42,** 1808 (1920); **47,** 684 (1925); **47,** 689 (1925); **48,** 326 (1926); *Z. physik. Chem.*, **117,** 1 (1926); HARNED and BRUMBAUGH, *J. Am. Chem. Soc.*, **44,** 2729 (1922); HARNED and STURGIS, *J. Am. Chem. Soc.*, **47,** 945 (1925); HARNED and SWINDELLS, *J. Am. Chem. Soc.*, **48,** 126 (1926); HARNED and JAMES, *J. Phys. Chem.*, **30,** 1060 (1926); HARNED and ÅKERLÖF, *Physik. Z.*, **27,** 411 (1926); ÅKERLÖF,

mining the activity coefficients of acids and bases in the presence of various salts, and their results for the activity coefficient of 0.1*m* hydrochloric acid in some chloride solutions at different concentrations of the salts are given in Table I.

TABLE I.—THE ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID (0.1*m*) IN THE PRESENCE OF OTHER CHLORIDES[a]

Total *m*	Pure HCl	HCl in LiCl	HCl in NaCl	HCl in KCl
0.1	0.81			
0.2	0.78	0.78	0.78	0.78
0.5	0.76	0.78	0.76	0.75
1.0	0.82	0.86	0.80	0.75
2.0	1.02	1.09	0.94	0.84
3.0	1.35	1.47	1.17	0.97
4.0	1.84	2.02	1.47	1.17

[a] LEWIS and RANDALL, "Thermodynamics," p. 367, McGraw-Hill Book Company, Inc., New York, 1923.

Although the concentration of the hydrochloric acid is held constant at 0.1*m* in the third, fourth, and fifth columns of Table I, nevertheless its activity coefficient goes through all the variations of the pure hydrochloric acid despite the fact that the increase in concentration of the solution is not due to added hydrogen chloride, but to added salt. An examination of the activity coefficient at 4.0*m* shows that the hydrochloric acid activity coefficient is higher in the lithium chloride solution than it is in the pure hydrochloric acid and lower in the potassium chloride solution than it is in the pure hydrochloric acid. All the chloride solutions of Table I have an ion in common with the hydrochloric acid, but it is not necessary for the added salts to have a common ion in order to affect the activity coefficient of the salt in question. As an illustration of this point, some data for the activity coefficient of thallous chloride in a number of electrolytes are given in Table II.

The presence of potassium nitrate diminishes the activity coefficient of the thallous chloride, although there is no common

J. Am. Chem. Soc., **48**, 1160 (1926); RANDALL and LANGFORD, *J. Am. Chem. Soc.*, **49**, 1445 (1927); RANDALL and BRECKENRIDGE, *ibid.*, **49**, 1435 (1927); HARNED and MASON, *ibid.*, **53**, 3377 (1931); **54**, 1439 (1932); HARNED and NIMS, *ibid.*, **54**, 423 (1932); HARNED and HECKER, *ibid.*, **56**, 650 (1934).

ion in this case to repress the dissociation of thallous chloride. (The thallous chloride is an insoluble salt; its maximum solubility in pure water at 25°C. is 0.016*c*.)

TABLE II.—ACTIVITY COEFFICIENT OF THALLOUS CHLORIDE AT 25°C.[a]

Total c	In KNO_3	In KCl	In HCl	In $TlNO_3$
0.001	0.970	0.970	0.970	0.970
0.002	0.962	0.962	0.962	0.962
0.005	0.950	0.950	0.950	0.950
0.01	0.909	0.909	0.909	0.909
0.02	0.872	0.871	0.871	0.869
0.05	0.809	0.797	0.798	0.784
0.1	0.742	0.715	0.718	0.686
0.2	0.676	0.613	0.630	0.546

[a] LEWIS and RANDALL, *op. cit.*, p. 372.

Classical Theory.—According to the classical dissociation theory of Arrhenius we can explain a decrease in the activity coefficient with increasing concentration by assuming that there is less dissociation at the higher concentrations, that the number of ions per mole declines with increasing concentration. According to this theory it would seem at first sight reasonable to consider the activity coefficient as being the same as the degree of dissociation as determined from conductance measurements (Chap. V). But if the activity coefficient and the degree of dissociation are compared, it is found that they are not the same, the difference between the two being particularly marked at the higher concentrations. Table III includes data for α and $\gamma_{\pm}$ for barium chloride at 25°C.

The lack of agreement between α and $\gamma_{\pm}$ does not surprise us for we have already learned in Chap. V that α is not a true measure of the degree of dissociation in the case of strong electrolytes such as barium chloride.

The classical dissociation theory is inadequate in interpreting the data of Table I or II in any quantitative way. Furthermore the unmodified theory is quite at a loss in trying to explain values of the activity coefficient or degree of dissociation greater than unity. An activity coefficient or degree of dissociation greater than unity has no meaning in the simple Arrhenius theory. Just as in the case of the interpretation of the electrical conductance of

electrolytes the classical theory here does not consider the interionic electrical attractions and so is in error. We must consider the effect that the Coulomb forces between the ions have upon the activity coefficient before we can arrive at a complete interpretation of the activity coefficient. First let us consider, however, the empirical discoveries that were made concerning the activity coefficient in the years preceding the Debye and Hückel theory.

TABLE III.—COMPARISON OF ACTIVITY COEFFICIENT AND DEGREE OF DISSOCIATION AT 25°C. AQUEOUS SOLUTIONS OF BARIUM CHLORIDE

m	$\alpha = \Lambda/\Lambda_0 \cdot \eta/\eta_0$	$\gamma_\pm$
0	1.000	1.000
0.0005	0.965	0.945
0.001	0.950	0.923
0.0025	0.921	0.867
0.005	0.892	0.801
0.01	0.858	0.716
0.025	0.808	0.631
0.05	0.767	0.563
0.1	0.727	0.492
0.25	0.681	0.420
0.5	0.653	0.387
1.0	0.634	0.373

Experimental Equations for the Activity Coefficient.—In our theoretical study of the conductance of solutions, the necessity of considering the electrical nature of the ions was strongly emphasized; we shall also find in this section that the value for the activity coefficient depends most importantly upon the electrical environment of the solutions. Bjerrum* at an early date made the statement that the activity coefficient of an ion was a function chiefly of "the *ion* concentration of the solution, the valence of the ions, and the dielectric constant of the solvent and only in a small degree of the remaining properties of the ions, for example, their weight and volume" [author's translation]. He found that an empirical equation of the form

$$-\log f_i = 26\frac{z_i}{D}\sqrt[3]{c_i}, \tag{1}$$

* Bjerrum, *Z. Elektrochem.*, **24**, 321 (1918).

where c_i is the ion concentration of the solution, f_i the ionic activity coefficient, z_i the valence of the ion, and D the dielectric constant of the solvent, agreed well with the experimental data in dilute solution.

Shortly after Bjerrum's important discovery, Brønsted* published a description of some interesting experiments in which the effect of the environment of the ions was well illustrated. If the deviation of the experimental results from the values predicted by the ideal equations based on the perfect gas laws is due to the electrical environment of the solution, it should be possible to eliminate this effect and to obtain data consistent with the ideal equations by carrying out experiments in which the concentration of the electrolyte was varied while at the same time the electrical nature of the solution was held constant. Brønsted accomplished this by measuring the e.m.fs. of cells containing cadmium ions at low concentrations in the presence of a large amount of magnesium sulfate. He set up a cell of the type

$$\begin{array}{c|c||c|c} \text{3.1\% Cd} & CdSO_4\ (c'') & CdSO_4\ (c') & \text{3.1\% Cd} \\ \text{amalgam} & MgSO_4\ (2\text{-}c'') & MgSO_4\ (2\text{-}c') & \text{amalgam} \end{array} \qquad (A)$$
$$a$$

in which the two solutions met at the liquid junction a; the liquid junction potential is in this case so small that it may be neglected (see Chap. XIX). The total concentration of both the solutions was held at $2c$; hence it is reasonable to assume that the electrical nature of both the solutions was the same. The concentration of cadmium sulfate varied from a maximum value of 0.1 to a minimum value of $\frac{1}{640}c$. The ratio of c' to c'' was always $\frac{1}{2}$ so that a constant e.m.f. equal to $0.058/2 \log \frac{2}{1}$, or 0.00881 v., should have been observed in all his measurements if the ideal equation

$$E = \frac{RT}{nF} \ln \frac{c''}{c'} \qquad (2)$$

is valid. Brønsted's results are given in Table IV. The average value of the data for the different concentrations is 0.00881 which deviates only five-hundredths of a millivolt from the ideal value, 0.00876 v. Hence Brønsted was able to conclude that "the gas laws hold good for ions or salts when other salt solutions are

* Brønsted, *Medd. k. Vet. Akad. Nobel Institut*, **5**, No. 25 (1919).

employed as solvents, the concentration of the latter being large when compared with the concentration of the dissolved ion or the dissolved salt." Brønsted's results are easy to explain on the

TABLE IV.—E.M.FS. OF THE CELL A AT 20°C.

c''	c'	E
1/10	1/20	0.00882
1/20	1/40	0.00887
1/40	1/80	0.00879
1/80	1/160	0.00873
1/160	1/320	0.00897
1/320	1/640	0.00860
		Average...... 0.00881

ideas of Bjerrum. The thermodynamic (exact) equation for the potential of cell (A) on introducing the ionic activity coefficient* $\mathbf{f}_i$ is

$$E = \frac{0.058}{2} \log \frac{c_i''\mathbf{f}_i''}{c_i'\mathbf{f}_i'}. \tag{3}$$

If, according to Bjerrum, the activity coefficient is a function primarily of the concentration and valence of the ions and of the dielectric constant, the activity coefficient of the cadmium ion must be the same in both the solutions, *i.e.*,

$$\mathbf{f}_i'' = \mathbf{f}_i', \tag{4}$$

since the number and valences of all the ions are the same in the two solutions. Equation (3) therefore becomes identical with the ideal equation and the experimental results agree with Eq. (2). This experiment of Brønsted, while not definitely proving the ideas of Bjerrum, nevertheless enabled Brønsted to state "with regard to the actually strong electrolytes N. Bjerrum and S. R. Milner have, however, advanced the assumption that these

* We are now introducing a third activity coefficient defined by Eq. (3) with the convention that $\mathbf{f}$ equals unity when c equals zero. In dilute solutions f, γ, and $\mathbf{f}$ are all equal or nearly equal to each other. For an extended discussion of activity coefficients and their definitions see Falkenhagen, "Electrolyte," pp. 54*ff*. S. Hirzel, Leipzig, 1932.

compounds in aqueous solution are completely dissociated, a view which would, of course, mean an essential simplification of our conception of the salt solutions, and which is also—as will be proved later—in the best accordance with the results. . . . "

A year later Brønsted* performed a very similar experiment in which he was able to calculate the number of undissociated molecules of magnesium chloride present in a solution 0.1 normal in chloride ions and 3.9 normal in magnesium sulfate. He measured e.m.f. values of the cell

$$\mathrm{Ag}\left|\,\mathrm{AgCl}\,\right|\begin{matrix}\mathrm{MgSO_4}(N - N'') \\ \mathrm{MgCl_2}(N'')\end{matrix}\left\|\begin{matrix}\mathrm{MgSO_4}(N - N') \\ \mathrm{MgCl_2}(N')\end{matrix}\right|\,\mathrm{AgCl}\,\left|\,\mathrm{Ag}\right. \qquad (B)$$

in which N' (the normality) was kept constant at 0.0032 equivalents of magnesium chloride per liter, N was kept constant at 4.0 normal, and N'' was varied from 0.016 to 4.00 equivalents per liter. At high concentrations of magnesium chloride one should not expect the observed e.m.fs. to agree with the ideal equation since the environment is changed due to the substitution of chloride ions for sulfate ions. Brønsted found that the deviations ΔE of the observed e.m.f. from the calculated e.m.f.

$$(E_{calcd.} - E_{obs.})$$

agreed with the equation,

$$\Delta E = 0.0037\,N''. \tag{5}$$

The mass action law as applied to the equilibrium

$$\mathrm{MgCl_2} \rightleftarrows \mathrm{Mg^{++}} + 2\mathrm{Cl^-}$$

is

$$\frac{c_{\mathrm{Mg^{++}}} \cdot c^2_{\mathrm{Cl^-}}}{c_{\mathrm{MgCl_2}}} = k' \tag{6}$$

or

$$\frac{c^2_{\mathrm{Cl^-}}}{c_{\mathrm{MgCl_2}}} = k, \tag{7a}$$

since in these experiments the concentration of the magnesium ion was kept constant. The concentration unit of Eq. (7*a*) is

* J. N. Brønsted, *Det. Kgl. Danske Videnskab. Selskab. Math.-fysik. Medd.*, III, No. 9 (1920).

moles per liter of solution. Introducing into Eq. (7*a*) the total chlorine concentration c, we have

$$\frac{c - c_{Cl^-}}{2} = \frac{c_{Cl^-}^2}{k}. \tag{7b}$$

According to the classical theory the observed e.m.f. will be given by the equation

$$E_c = 0.0581 \log \frac{c''_{Cl^-}}{c'_{Cl^-}} \tag{8a}$$

whereas the ideal equation is

$$E_i = 0.0581 \log \frac{c''}{c'}. \tag{8b}$$

Since, by this theory,

$$\Delta E = E_i - E_c,$$

and since c' in the dilute solution can be assumed to be equal to c'_{Cl^-} (*i.e.*, we assume complete dissociation of $MgCl_2$ in the dilute solution),

$$\Delta E = 0.0581 \log \frac{c''}{c''_{Cl^-}} \tag{9a}$$

or

$$\Delta E = 0.0581 \log \left(\frac{4c''}{-k + \sqrt{k^2 + 8kc''}} \right) \tag{9b}$$

on eliminating c''_{Cl^-} by means of Eq. (7*b*). By the insertion of $c = 0.1$ and $\Delta E = 0.00037$ into this equation, k is calculated to be equal to 13.3. Values of ΔE calculated from Eq. (9*b*) using this value of k are in good agreement with the data, and it would appear that the classical theory is substantiated. If, however, the concentration of the undissociated magnesium chloride is calculated by means of Eq. (7*a*) at a concentration of $c = 0.1$, the concentration turns out to be only 0.0007 mole per liter. This result is rather astounding inasmuch as it indicates that only 0.7 per cent of the total chlorine is in the form of magnesium chloride despite the excess amount of magnesium present. In other words, the magnesium chloride is very nearly completely dissociated under these conditions. This unexpected result is further confirmation of Bjerrum's hypothesis that the deviations in the behavior of strong electrolytes are to be explained on the

basis of electrical effects rather than on the basis of a partial dissociation varying with the concentration.

The necessity of considering the electrical constitution of the solution was also clearly brought out by the discovery by Lewis and Randall* of an important rule called by them the *principle of the ionic strength.* If the data in Table II are examined, it will be noticed that the activity coefficient of the thallous chloride is practically identical in all of the different solutions studied up to a concentration of about 0.02c. This correspondence in the values of the activity coefficient led Lewis and Randall to enunciate the following simple rule: "In any dilute solution of a mixture of strong electrolytes of the same valence type, the activity coefficient of each electrolyte depends solely upon the total concentration." In other words, it does not matter what uniunivalent salt is present in the solution; the thallous chloride will have the same activity coefficient at the same total concentration of the solution. This rule is only applicable to dilute solutions, however; at a concentration of 0.2 N the activity coefficient of thallous chloride varies from 0.546 in thallous nitrate to 0.676 in potassium nitrate.

Lewis and Randall went further in their study of the activity coefficient and discovered the important principle of the ionic strength. The principle of ionic strength as stated by them is as follows: "In dilute solutions, the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength." They define the ionic strength μ as equal to one half of the sum of the products of the concentration of each ion multiplied by the square of its valence, or

$$\mu = \tfrac{1}{2}\sum_i c_i z_i^2, \tag{10}$$

where c_i is the ionic concentration in moles per liter of solution.†

* LEWIS and RANDALL, *J. Am. Chem. Soc.*, **43**, 1112 (1921).

† Lewis and Randall define the ionic strength in terms of moles per 1,000 g. of water instead of moles per liter of solution. For reasons that appear in the next chapter it is necessary here to define the ionic strength in terms of moles per liter of solution. At low concentrations, where the ionic-strength principle is only valid, these two concentration units practically coincide. The ionic concentration is assumed to be equal to the stoichiometrical concentration of the ions for strong electrolytes.

If the solution contains but two kinds of ions, the ionic strength may also be expressed by the equation

$$\mu = \tfrac{1}{2} N(z_1 + z_2), \tag{11}$$

where N is the normality of the solution. In order to understand the significance of the ionic strength and the relation of the ionic strength to the stoichiometrical concentration, values of both are compared in Table V for a number of electrolytes.

TABLE V.—COMPARISON OF CONCENTRATION AND IONIC STRENGTH

Solution	Total concentration, moles per liter	Ionic strength
0.1 N KCl	0.1	0.1
0.1 N $BaCl_2$	0.05	0.15
0.1 N $Al_2(SO_4)_3$	0.01666	0.25
0.1 N $Ba_2Fe(CN)_6$	0.025	0.30
0.0666 N $BaCl_2$	0.0333	0.1
0.04 N $Al_2(SO_4)_3$	0.006666	0.1
0.1 N KCl, 0.1 N $BaCl_2$	0.15	0.25

For uniunivalent electrolytes like potassium chloride the concentration and the ionic strength are identical, but as the valence of either the positive or the negative ions becomes greater than 1, the ionic strength becomes greater than the concentration. The principle of Lewis and Randall states that the activity coefficient of a particular electrolyte will be the same in solutions having identical ionic strengths. Thus the activity coefficient of thallous chloride should be the same in a 0.1c potassium chloride solution as it is in a 0.0333c barium chloride solution or as it is in a 0.00666c aluminum sulfate solution since these three solutions all have the same ionic strength.

The importance of the discovery of Lewis and Randall was made evident soon afterward by the publication of the well-known paper of Brønsted and La Mer,* who determined the activity coefficients of some insoluble substances in the presence of a number of electrolytes. Although their method was not an electrochemical method, their results are applicable to the present discussion since the activity coefficient of a substance in a

* BRØNSTED and LA MER, *J. Am. Chem. Soc.*, **46**, 555 (1924).

solution is independent of the method used to determine it; furthermore, their data are particularly suitable to test the Lewis and Randall principle of ionic strength because the measurements were performed on dilute solutions where the observed phenomena are not so complicated as they are in concentrated solutions. In Table VI are given values of the activity coefficient of two complex cobalt amines of different valence types in a number of electrolytes at a total ionic strength of approximately 0.01.

TABLE VI.—ACTIVITY COEFFICIENTS AT 25°C OF TWO PARTIALLY SOLUBLE SALTS IN VARIOUS SOLUTIONS

Solvent solution	$NaCl$	KNO_3	$MgSO_4$	$K_3Co(CN)_6$	
Saturating salt $[Co(NH_3)_4C_2O_4]^+[Co(NH_3)_2(NO_2)_2C_2O_4]^-$					Ionic strength =0.01054
Solvent salt, normality	0.010	0.010	0.0050	0.0050	
Saturating salt, activity coefficient	0.885	0.881	0.876	0.856	
Saturating salt $[Co(NH_3)_4C_2O_4]_2^+[S_2O_6]^-$					ionic strength = 0.01056
Solvent salt, normality	.....	0.010	0.0005	0.0050	
Saturating salt, activity coefficient	.....	0.780	0.786	0.777	

It is readily seen that the activity coefficient of the uniunivalent cobalt amine is nearly the same in all four solutions, but because of the difference in valence its activity coefficient is considerably higher than the activity coefficient of the unibivalent cobalt amine. There are many more data which might be tabulated or plotted in support of the Lewis and Randall ionic-strength principle, but they will not be introduced at this point as it will be more interesting to consider the data not only in the light of the ionic-strength principle but also with respect to the more general theoretical equations of Debye and Hückel.

CHAPTER XVIII

THEORETICAL INTERPRETATION OF THE ACTIVITY COEFFICIENTS OF ELECTROLYTES

II. MATHEMATICAL THEORY OF DEBYE AND HÜCKEL

The application of the interionic attraction theory of Debye and Hückel to the calculation of the variation of the activity coefficient with concentration is much shorter and simpler than the corresponding conductance calculation as carried out by Onsager; hence it will be possible to describe Debye and Hückel's calculation in detail.

As before we consider first of all the electrical nature of the ions in solution. Making the assumption that electrical forces exist between the ions in accordance with Coulomb's law, Debye and Hückel* postulate that on the time average there are more ions of unlike sign around an ion than of like sign. About each ion the other ions of the solution tend to group themselves in a symmetrical arrangement; the Brownian motion or thermal vibration of the ions will tend to distribute the ions in a perfectly random manner and will thus oppose the tendency of the ions to group themselves symmetrically. Nevertheless, there will result a certain preferred orientation of ions about each other, a distribution of ions which is called the "ionic atmosphere" about an ion. The ionic atmosphere about an ion is always of such a nature that it produces in the location occupied by the ion a potential of opposite sign to the ion. To illustrate this significant conclusion we may cite the example of potassium chloride in water. There will be more chloride ions in the neighborhood of each potassium ion than there are other potassium

* DEBYE and HÜCKEL, *Physik. Z.*, **24**, 185 (1923); see also A. A. NOYES, *J. Am. Chem. Soc.*, **46**, 1080 (1924); E. HÜCKEL, *Erg. d. exakten Naturwissensch.*, **3**, 199 (1924); V. K. LA MER, *Trans. Amer. Electrochem. Soc.*, **51**, 507 (1927); H. FALKENHAGEN, *Rev. Mod. Phys.*, **3**, 412 (1931); "Elektrolyte" S. Hirzel, Leipzig, 1932 (English translation by Bell, 1934).

ions, and if we were to remove the potassium ion under consideration from the solution and if we could measure the electrical potential which would exist in the empty space caused by the removal of the potassium ion, we should find the potential to be negative in sign. Hence we can state that work must be done on the system in order to remove a potassium ion from the electrical attraction of its ionic atmosphere.

In the conductance theory of Debye and Onsager we were interested chiefly in the distortion of the ionic atmosphere as the ion migrates through the solution, but in the theory for the activity coefficient an unsymmetrical ionic atmosphere does not exist, as the ions are stationary (the ions are moving due to Brownian motion, but they have no net displacement in any direction). We have to deal, therefore, with a stationary ionic atmosphere. The ionic atmosphere has no definite dimensions. It may be considered as extending indefinitely away from the central ion; however, it will be possible to calculate the effective "thickness" of the ionic atmosphere, *i.e.*, it will be possible to say that the atmosphere acts as if it were located a certain distance away from the ion. Later on we shall calculate this distance and demonstrate how the ionic atmosphere varies with concentration, temperature, etc.

The potential at an electrode immersed in a solution of its ions is a measure of the tendency of an ion to "escape" from the solution or of the tendency of a solution to dilute itself. A dilute sugar solution, for example, will dilute itself if brought in contact with pure water; the free energy of dilution can be calculated in this ideal case from the equations applicable to perfect solutions. But a dilute solution of ions does not have so great a tendency to dilute itself as it would were the ions uncharged because the ionic atmosphere about each ion tends to "hold" the ion in the solution. Hence the potential at the electrode which is a measure of the free energy of dilution will be modified by the electrical forces between the ions. If the solution is a perfect solution, the activity coefficients of the ions are equal to unity, and the observed potential obeys the ideal equation. Actually, we know that the solution is not ideal and that the activity coefficient in dilute solutions becomes less than unity. Now Debye and Hückel make the assumption that the entire

deviation of the activity coefficient from unity is due to the ionic atmosphere about an ion. They assert that the electrical forces between the ions are the chief causes for the lack of ideality in solutions of strong electrolytes, and by calculating the effect of the interionic attractions on the free energy of dilution they are able to derive an equation expressing the deviation of the activity coefficient from unity. Thus, Debye and Hückel's mathematical treatment may be briefly reviewed as follows: The electrical potential in the place of a central ion due to the ion's "ionic atmosphere" is first determined, the work of removing the ion from the solution against the attractive force of the ionic atmosphere is next calculated, and after summing up this work for both positive and negative ions, the equation for the activity coefficient is readily derived. The significant contribution of Debye and Hückel is the calculation of the electrical potential in the place of the ion. Let us see how they were able to solve the problem for this long-sought-for unknown.

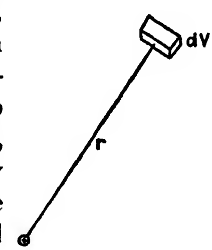

FIG. 1.

Consider a small volume dV of solution in the neighborhood of a positive ion (Fig. 1). According to the principles of the Debye theory there will be on the time average more negative ions in dV than there are positive ions, owing to the presence of the positive ion at the distance r from dV. If the time-average value of the electrical potential in the volume element is ψ, the work which must be performed on a positive ion to bring it from infinity to dV is $z_+\epsilon\psi$ and for a negative ion $-z_-\epsilon\psi$. Debye and Hückel first make use of the Maxwell and Boltzmann distribution law which for positive ions is

$$n_+ = ne^{-\frac{z_+\epsilon\psi}{kT}} \tag{1}$$

and for the negative ions

$$n_- = ne^{+\frac{z_-\epsilon\psi}{kT}}. \tag{2}$$

In Eqs. (1) and (2) n_+ and n_- are the number of positive and negative ions, respectively, per cubic centimeter, n is the stoichiometrical concentration of these ions per cubic centimeter, z is the valence of the ion (always to be taken as a positive number),

ϵ is the unit positive charge, ψ is the electrical potential at the location under consideration, k is the Boltzmann constant, and T is the absolute temperature.

The statistical derivation of Eq. (1) is rather long and beyond the scope of this book. However, it is possible that the following discussion may give some idea concerning the significance of the equation. Debye and Hückel made use of Einstein's equation for the Brownian movement in their conductance theory. This equation is

$$\rho_i\left(\frac{dn_i}{d\tau}\right) = \text{div } (kT \text{ grad } n_i - n_i q_i \mathbf{E} + n_i q_i \text{ grad } \psi), \tag{3}$$

where ρ_i is the friction coefficient of the ion, $\mathbf{E}$ is the externally applied field, and τ is the time. In the activity coefficient theory the number of ions per cubic centimeter does not vary with time nor is there an applied external field, so we can set both $\mathbf{E}$ and $dn_i/d\tau$ equal to zero and write

$$kT \frac{\text{div grad } n_i}{n_i} = -q_i \text{ div grad } \psi, \tag{4}$$

or on integration

$$kT \ln n_i = -q_i\psi + \text{const.}$$

or

$$n_i = (\text{const.})\, e^{-\frac{q_i\psi}{kT}}. \tag{5}$$

In our case the constant is obviously equal to the stoichiometrical concentration; hence

$$n_i = ne^{-\frac{q_i\psi}{kT}} \tag{6}$$

in agreement with Eq. (1). In Eqs. (3) to (6) q_i is negative for a negative ion.

Multiplying Eq. (1) by dV, we get

$$n_+ dV = ne^{-\frac{z_+\epsilon\psi}{kT}} dV \tag{7}$$

and

$$n_- dV = ne^{\frac{z_-\epsilon\psi}{kT}} dV. \tag{8}$$

It is interesting to study the properties of the Maxwell and Boltzmann distribution law before going further with the

mathematical treatment. If the central ion of Fig. 1 is uncharged, there will be no potential due to this ion in the volume element, $\psi = 0$; hence

$$n_+ dV = n dV \tag{9}$$
$$n_- dV = n dV. \tag{10}$$

If the ions, or better particles, in dV are uncharged, $z\epsilon = 0$, then again Eqs. (9) and (10) are valid and the distribution of the particles is perfectly random. If the temperature becomes infinite, $z\epsilon\psi/kT$ becomes equal to zero and in this case the distribution is given by Eqs. (9) and (10) so that the distribution will be completely random if the ions are uncharged, if the temperature becomes infinite, or if they are so far apart that the potential in dV, ψ is zero. As the value of the exponent $z\epsilon\psi/kT$ deviates from zero, the excess of positive or negative ions in dV becomes greater; hence increase of the potential in dV due to the central positive ion in Fig. 2, increase of valence of the ions, and decrease of the temperature will all cause the distribution of the ions to be less random and will bring about greater deviations from the behavior characteristic of perfect solutions.

From Eqs. (7) and (8) it is easy to derive a value for the density of electricity in the volume element dV. The density of electricity Π, is simply the excess positive or negative electricity per unit of volume, and in the case under discussion is given by the equation

$$\Pi = \frac{n_+\epsilon dV - n_-\epsilon dV}{dV} = n\epsilon\left(e^{-\frac{\epsilon\psi}{kT}} - e^{\frac{\epsilon\psi}{kT}}\right) \tag{11}$$

for a uniunivalent electrolyte, or in general,

$$\Pi = \epsilon\sum_i n_i z_i e^{-\frac{z_i\epsilon\psi}{kT}}. \tag{12}$$

[In Eq. (12) the valence z is to be taken as negative for anions. Unless stated to the contrary a negative valence should be taken in this book as positive.] Equation (12) must be solved for ψ, but inasmuch as there are two unknowns in Eq. (12), we must introduce another equation relating the potential and the electrical density. At this point Debye and Hückel made use of the well-known Poisson equation which is

$$\Delta\psi = -\frac{4\pi\Pi}{D}, \tag{13}$$

where D is the dielectric constant of the medium and $\Delta\psi$ is equal to

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} \tag{14}$$

in Cartesian coordinates. In polar coordinates

$$\Delta\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}. \tag{15}$$

Equation (15) can fortunately in the present derivation be simplified to

$$\Delta\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) \tag{16}$$

because the potential about an ion is spherically symmetrical. This means that $\partial\psi/\partial\theta$ and $\partial\psi/\partial\phi$ are both zero. The Poisson equation may be simply derived in the following way:* Imagine a solid sphere filled with electricity uniformly distributed throughout. The potential at a point p, Fig. 2, is given by the equation (which assumes Coulomb's law).

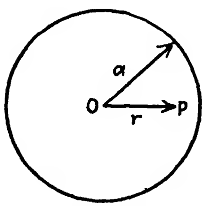

Fig. 2.

$$\psi = 2\frac{\pi\Pi a^2}{D} - \frac{2}{3}\frac{\pi\Pi r^2}{D}. \tag{17}$$

If we assume that the center of the Cartesian coordinate system is at O, then

$$r^2 = x^2 + y^2 + z^2. \tag{18}$$

Differentiating Eq. (17) with respect to x we obtain

$$\frac{\partial\psi}{\partial x} = -\frac{4}{3}\frac{\pi\Pi r}{D}\frac{\partial r}{\partial x}. \tag{19}$$

But from Eq. (18)

$$\frac{\partial r}{\partial x} = \frac{x}{r}; \tag{20}$$

hence

$$\frac{\partial\psi}{\partial x} = -\frac{4}{3}\frac{\pi\Pi x}{D}. \tag{21}$$

* Jäger, "Theoretische Physik," Vol. III, p. 12.

A second differentiation gives

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{4}{3}\frac{\pi \Pi}{D}; \tag{22}$$

similarly

$$\frac{\partial^2 \psi}{\partial y^2} = -\frac{4}{3}\frac{\pi \Pi}{D} \tag{23}$$

and

$$\frac{\partial^2 \psi}{\partial z^2} = -\frac{4}{3}\frac{\pi \Pi}{D}. \tag{24}$$

Adding Eqs. (22), (23), and (24), we obtain the desired relationship (13). Equation (13) may be easily arrived at by introducing Eq. (17) into (16).

Before eliminating the electrical density from Eqs. (11) and (13), let us simplify Eq. (11) by expanding the exponential functions in a power series and dropping off all terms higher than the first. Since

$$[e^{-x} - e^{x}] = -2x - \frac{2x^3}{3!} - \frac{2x^5}{5!} - \frac{2x^7}{7!} \cdots, \tag{25}$$

we have

$$\Pi = -2n\frac{\epsilon^2\psi}{kT} - \frac{2n\epsilon^4\psi^3}{3!\,k^3T^3} - \frac{2n\epsilon^6\psi^5}{5!\,k^5T^5} \cdots. \tag{26}$$

Disregarding all terms in ψ above the first power, the value for the electrical density becomes

$$\Pi = -2\frac{n\epsilon^2\psi}{kT}. \tag{27}$$

Such an approximation is only valid when $\epsilon\psi/kT$ is very much smaller than 1 (mathematically expressed, $\epsilon\psi/kT << 1$). The conditions best suited for making this assumption are: The solutions must be dilute so that ψ is small, the ions must be uniunivalent ions so that $z\epsilon$ is as small as possible and finally the temperature must not be too low. The general form for Eq. (27) is

$$\Pi = \epsilon\sum_i n_i z_i - \frac{\epsilon^2\psi}{kT}\sum_i n_i z_i^2. \tag{28}$$

Since the total charge must be zero, it follows that

$$\epsilon\Sigma n_i z_i = 0 \tag{29}$$

(z_i is negative for a negative valence here).
Eliminating Π from Eqs. (27) and (13), we get

$$\Delta\psi = \frac{8\pi n\epsilon^2\psi}{DkT} = \kappa^2\psi, \tag{30a}$$

or for the general case

$$\Delta\psi = \frac{4\pi\epsilon^2\psi}{DkT}\sum_i n_i z_i^2 = \kappa^2\psi. \tag{30b}$$

The quantity κ is defined by the equation

$$\kappa^2 = \frac{8\pi n\epsilon^2}{DkT}, \tag{30d}$$

or for the general case

$$\kappa^2 = \frac{4\pi\epsilon^2}{DkT}\sum_i n_i z_i^2. \tag{30e}$$

κ is an important quantity in the Debye theory because it is a measure of the thickness of the ionic atmosphere as will be shown later. Since n is the number of ions per cubic centimeter, it is evident that κ is proportional to the square root of the concentration, and as a consequence the effect of the interionic attractions as calculated by Debye turns out to be proportional to the square root of the concentration in the cases of the conductance change, the change in viscosity, and the change in the logarithm of the activity coefficient.

Continuing with the mathematical development, we can immediately write down the general solution for the integration of Eq. (30a) as

$$\psi = A\frac{e^{-\kappa r}}{r} + A'\frac{e^{+\kappa r}}{r}. \tag{31}$$

That Eq. (31) is a solution of Eq. (30a) can readily be proved by setting this value of ψ back into Eq. (30a). In so doing it is more convenient to write Eq. (30a) in the following form:

$$\Delta\psi = \frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r} = \kappa^2\psi. \tag{30c}$$

The value of ψ must vanish when r becomes equal to infinity; hence the constant A' of Eq. (31) must be equal to zero. To

evaluate A it is only necessary to realize that in *very dilute solutions* the potential in the immediate neighborhood of the ion must be due solely to the ion in question. If we may consider the ion as a point charge, the potential at small distances from the ion is equal to ϵ/Dr; hence as r becomes small, Eq. (31) should reduce to this value. This can be true if the A constant is equal to ϵ/D; hence Eq. (31) becomes

$$\psi = \frac{\epsilon}{D}\frac{e^{-\kappa r}}{r}, \tag{32a}$$

or in general

$$\psi = \frac{z_i\epsilon}{D}\frac{e^{-\kappa r}}{r}. \tag{32b}$$

(Here take z negative for anions).* We can now separate ψ into two parts, ψ_{I}, the potential due to the central ion under consideration uninfluenced by other ions, and ψ_{II}, the potential due to the ionic atmosphere of the central ion. Since

$$\psi_{\text{I}} = \frac{\epsilon}{Dr}, \tag{33}$$

then

$$\psi_{\text{II}} = -\frac{\epsilon}{D}\left(\frac{1 - e^{-\kappa r}}{r}\right), \tag{34}$$

for

$$\psi = \psi_{\text{I}} + \psi_{\text{II}}.$$

What we are interested in is the potential ψ_i due to the ionic atmosphere of the central ion at the location of the ion in question. This is readily obtained by setting r equal to zero in Eq. (34) after we have expanded the exponential term into a series, *e.g.*,

$$\psi_{\text{II}} = -\frac{\epsilon}{D}\left(\frac{1}{r} - \frac{1}{r} + \frac{\kappa r}{r} - \frac{\kappa^2 r^2}{2!\,r} \cdots\right),$$

and

$$\psi_i = -\frac{\epsilon\kappa}{D}; \tag{35a}$$

* Expanding Eq. (32*a*) we get

$$\psi = \frac{\epsilon}{D}\frac{1}{r}\left(1 - \kappa r + \frac{\kappa^2 r^2}{2!} \cdots\right);$$

when r becomes very small, this expression reduces to $\psi = \epsilon/Dr$.

or in general

$$\psi_i = -\frac{z_i \epsilon \kappa}{D}. \tag{35b}$$

In Eq. (35b) z_i is negative for a negative ion and is the valence of the central ion; hence it is evident that the potential due to the other ions at the location of the central ion always has an opposite sign to the ion in question. The importance of κ is understood on examination of Eq. (35) because this equation tells us that a single ion of equal but opposite charge at a distance $1/\kappa$ away from the central ion would produce the same potential at the location of the central ion as is produced by the ionic atmosphere about the ion. Hence it is convenient to think of the ionic atmosphere as being located at the distance $1/\kappa$ away from the ion, although in reality the ionic atmosphere is spread over the whole solution.

The dependence of $1/\kappa$ upon the concentration, valence of the ions, dielectric constant of the solvent, and temperature may be estimated by studying Eq. (30e). Actually $1/\kappa$ has the values given in Table I for the special case of 0.001 molal solutions in water at 18°C.*

TABLE I.—THICKNESS OF THE IONIC ATMOSPHERE, $1/\kappa$, 0.001 c AQUEOUS SOLUTIONS AT 18°C.

Valence type of electrolyte	Thickness, $1/\kappa$, Cm.
1–1	96.6×10^{-8}
1–2	55.9×10^{-8}
2–2	48.4×10^{-8}
1–3	39.5×10^{-8}
1–4	30.4×10^{-8}
2–4	27.8×10^{-8}

It is an easy matter to go from Eq. (35) to the equation for the activity coefficient. It will be remembered that the actual process whose free energy is measured in a galvanic cell is a transfer of molecules of the solute from one concentration to another, the two solutions being present in such a large amount that the concentrations are not altered. This process is physically different from the process of dilution in which the concentration of a definite amount of solution is gradually decreased to a smaller value. The process of transfer signifies that the ions are

* H. FALKENHAGEN, "Elektrolyte," p. 105, S. Hirzel, Leipzig, 1932.

removed from the solution without affecting the potential in the place of the ion due to its ionic atmosphere, whereas the process of dilution requires the potential also to change.

The chemical potential of a single ion in a *perfect* solution is

$$\mu_i = K + kT \ln N_i, \tag{36}$$

where K is a constant, depending only on the temperature and pressure. For a nonideal solution it is necessary to introduce the activity coefficient, *viz.*,

$$\mu_i = K + kT \ln N_i + kT \ln f_i. \tag{37}$$

It is the chief argument of Debye and Hückel that the term $kT \ln f_i$ is due entirely to the electrical energy of the ion in the solution which is simply (from the principles of electrostatics)*

$$\tfrac{1}{2}\epsilon\psi_i \tag{38}$$

or

$$-\frac{\epsilon^2\kappa}{2D}$$

after introduction of the value for ψ_i as given by Eq. (35*a*); hence we obtain as the equation for the chemical potential according to the Debye and Hückel theory

$$\mu_i = K + kT \ln N_i - \frac{\epsilon^2\kappa}{2D}. \tag{39}$$

* This expression for the energy of the system per ion may be derived in the following way (see PAGE and ADAMS, "Principles of Electricity," p. 69, D. Van Nostrand Company, Inc., New York, 1931): Let us assume that we have an isolated conductor which we wish to charge with an amount of electricity equal to ϵ. The charging of the conductor requires the expenditure of a certain amount of energy which will be stored electrostatically and which will become available again when the system is discharged. The potential of an isolated conductor is proportional to its charge so that at any time

$$q = k\psi.$$

Bringing an infinitesimal charge dq from infinity to the conductor does not change the potential ψ by a finite amount, and the potential energy of this process is ψdq. If the final charge is ϵ and the final potential ψ_i, the energy of the charged conductor is

$$U_e = \int_0^\epsilon \psi dq = \frac{1}{k}\int_0^\epsilon q dq = \frac{1}{2}\frac{\epsilon^2}{k} = \frac{1}{2}\epsilon\psi_i.$$

in agreement with Eq. (38).

From Eqs. (37) and (39) we obtain as the desired theoretical equation for the activity coefficient

$$\ln f_i = -\frac{\epsilon^2\kappa}{2DkT}. \tag{40a}$$

In the general case

$$\ln f_i = -\frac{z_i^2\epsilon^2\kappa}{2DkT}. \tag{40b}$$

Experimental Verification of the Debye and Hückel Equation.—Before testing Eq. (40) it is necessary to introduce the molal concentration. From Eq. (30*e*).

$$\kappa = \sqrt{\frac{4\pi\epsilon^2}{DkT}\sum_i n_i z_i^2},$$

but the number of ions per cubic centimeter may be replaced by the quantity

$$n_i = \frac{\mathbf{N}c_i}{1{,}000}, \tag{41}$$

where $\mathbf{N}$ is Avogadro's number (6.06×10^{23}). The activity-coefficient equation becomes

$$\ln f_i = -\frac{z_i^2\epsilon^3}{(DkT)^{3/2}}\sqrt{\frac{\pi\mathbf{N}}{1{,}000}\sum_i c_i z_i^2}. \tag{42}$$

Thus we see that according to this theory the activity coefficient is a function of the temperature, dielectric constant of the solvent, valence, and concentration of the ions in the solution. Is this in agreement with experiment?

In the first place Eq. (42) is in entire agreement with the conclusion reached by Bjerrum in 1918 that the activity coefficient is a function chiefly of "the *ion* concentration of the solution, the valence of the ions, and the dielectric constant of the solvent." The experimental work of Brønsted, as quoted in Table IV, Chap. XVII, is also in entire harmony with the Debye and Hückel theory. Furthermore Eq. (42) gives directly a theoretical explanation of the two rules enunciated by Lewis and Randall "in any dilute solution of a mixture of strong electrolytes of the same valence type, the activity coefficient of each elec-

trolyte depends solely upon the total concentration" and "in dilute solutions, the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength." It will be remembered that Lewis and Randall define the ionic strength as

$$\mu = \tfrac{1}{2}\Sigma c_i z_i^2, \qquad \text{(XVII–10)}$$

whereas the quantity $\Sigma c_i z_i^2$ occurs in Eq. (42); since the latter is exactly twice the ionic strength, it is immediately evident that the Debye and Hückel theory provides a theoretical interpretation for the principle of the ionic strength experimentally discovered by Lewis and Randall.

But it is possible to test Eq. (42) quantitatively. Fortunately Eq. (42) contains no constant which must be determined from the data for the activity coefficient; hence it is possible to test the Debye and Hückel theory without introducing any empirical or adjustable constants. The equation for the activity coefficient of a binary salt as a whole is

$$\ln f_{\pm} = -\frac{(\nu_+ z_+^2 + \nu_- z_-^2)}{\sum_i \nu_i} \frac{\epsilon^3}{(DkT)^{3/2}} \sqrt{\frac{\pi N}{1{,}000} \sum_i c_i z_i^2},$$

or

$$\ln f_{\pm} = -z_+ z_- \frac{\epsilon^3}{(DkT)^{3/2}} \sqrt{\frac{\pi N}{1{,}000} \sum_i c_i z_i^2}. \qquad (43)$$

The constants in Eq. (43) have the following numerical value:*

$\epsilon = (4.770 \pm 0.005) \times 10^{-10}$ e.s.u. $= 4.77 \times 10^{-10}$
$\mathbf{N} = (6.064 \pm 0.006) \times 10^{23}$ mole^{-1} $= 6.06 \times 10^{23}$
$k = (1.3708 \pm 0.0014) \times 10^{-16}$ erg deg^{-1} $= 1.37 \times 10^{-16}$
$T = 273.18 \pm t$°C.

The dielectric constant of water at 25°C. is 78.5 according to the measurements of Drake, Pierce, and Dow and of Wyman.† Substituting these values into Eq. (43), we obtain for 25°C. after converting from natural logarithms to Briggsian logarithms:

* R. T. Birge, *Rev. Mod. Phys.*, **1**, 1, (1929).

† Drake, Pierce, and Dow, *Phys. Rev.*, **35**, 613 (1930); Wyman, *Phys. Rev.*, **35**, 623 (1930).

$$\log f_{\pm} = -0.358 z_+ z_- \sqrt{\sum_i c_i z_i^2}, \tag{44}$$

or for a uniunivalent electrolyte

$$\log f_{\pm} = -0.506\sqrt{c}. \tag{45}$$

In Eq. (45) c is the stoichiometrical concentration; hence at this point we have made the important assumption that the *ionic* concentration is identical with the stoichiometrical concentration, *i.e.*, we assume complete dissociation. For this reason the theory of Debye and Hückel is sometimes called "the theory of complete dissociation," but this is incorrect inasmuch as Eq. (44) may be applied to acetic acid solutions where it is unnecessary and impossible to make the assumption of complete dissociation. Indeed, one of the most conclusive verifications of Eq. (44) recently announced by MacInnes and Shedlovsky* was based upon the application of this equation to acetic acid solutions. By a method to be described later (Chap. XX), MacInnes and Shedlovsky were able to prove that Eq. (44) agrees almost exactly with the conductance data (as applied to the calculation of the mass action constant) up to a stoichiometrical acetic acid concentration equal to approximately 0.005c. MacInnes and Shedlovsky conclude "in fact the data corresponding to solutions of acetic acid below 0.01 N are in quantitative agreement with the theory."

Hall† has tested Eq. (45) with some data obtained by Carmody for the activity coefficient of hydrochloric acid solutions calculated from e.m.f. data. For the ratio $-(\log f_{\pm})/\sqrt{c}$ between the concentrations 0.005 and 0.0003c Hall calculates from the data the following values: 0.47, 0.45, 0.43, 0.45, 0.47, 0.47, and 0.47. Considering the experimental difficulties in obtaining reliable e.m.f. data below 0.01c these results are in satisfactory agreement with the theoretical constant, 0.506. Falkenhagen‡ quotes the figures of Table II in support of the Debye theory.

* D. A. MacInnes and T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1429 (1932).

† N. F. Hall, *J. Am. Chem. Soc.*, **54**, 831 (1932). See also Wynne-Jones, *ibid.*, **54**, 2130 (1932); Carmody, *ibid.*, **54**, 188 (1932).

‡ Falkenhagen, "Elektrolyte," p. 130, S. Hirzel, Leipzig, 1932.

TABLE II.—ACTIVITY COEFFICIENT OF THE UNIUNIVALENT COMPLEX COBALT SALT, COBALT NITROTHIOCYANATE AT 15°C. IN AQUEOUS SOLUTIONS OF SODIUM CHLORIDE

Concn. of NaCl	$f_{\pm}(obs.)$	$f_{\pm}(calc.)$	Diff.
0.	0.980	0.979	0.001
0.0003	0.975	0.971	0.004
0.0010	0.965	0.959	0.006
0.0020	0.952	0.946	0.006
0.0100	0.906	0.890	0.016
0.0200	0.867	0.848	0.019

Just as we found in the case of the conductance of solutions, the theoretical values of the activity coefficients deviate from the observed more and more as the concentration is raised. This is not surprising in view of the approximations made in the simplification of the mathematical treatment. However, we may conclude that the Debye and Hückel equation correctly predicts the value of the ratio $-(\log f_{\pm})/\sqrt{c}$ to which the data approach as the concentration is diminished. This is true, at least, for uniunivalent salts in aqueous solution. Baxter* has also shown that Eq. (43) is verified at 75°C. In other words, the Debye and Hückel theory correctly accounts for the temperature variation of the activity coefficient. Let us now turn our attention to the study of salts of higher valence type and to nonaqueous solutions. For this purpose we shall make use of the results published in the paper of Brønsted and La Mer.† They measured the activity coefficient of the following difficultly soluble salts in the presence of various electrolytes:

1–1 valence type $[Co(NH_3)_4(NO_2)(CNS)][Co(NH_3)_2(NO_2)_2C_2O_4]$

1–2 valence type $[Co(NH_3)_4(C_2O_4)]_2S_2O_6$

3–1 valence type $[Co(NH_3)_6][Co(NH_3)_2(NO_2)_2(C_2O_4)]_3$,

and obtained the results plotted in Fig. 3. The solid lines represent the theoretical values predicted by the equation, and it is easily seen that the experimental results agree for the most part rather closely with the predicted straight lines. The logarithm

* W. P. BAXTER, *J. Am. Chem. Soc.*, **48**, 615 (1926).

† BRØNSTED and LA MER, *J. Am. Chem. Soc.*, **46**, 555 (1924).

of the activity coefficient is plotted against the square root of the ionic strength. More recent results of La Mer, King, and Mason* indicate that the activity coefficients of the 3–3 valence type salt

$$[Co(NH_3)_6][Fe(CN)_6]$$

are less than the theoretical values in dilute solutions of all salts having a negative valence greater than 1, *i.e.*, potassium sulfate, magnesium sulfate, potassium ferro- and ferricyanide, and are greater than theoretical values in dilute solutions of potassium

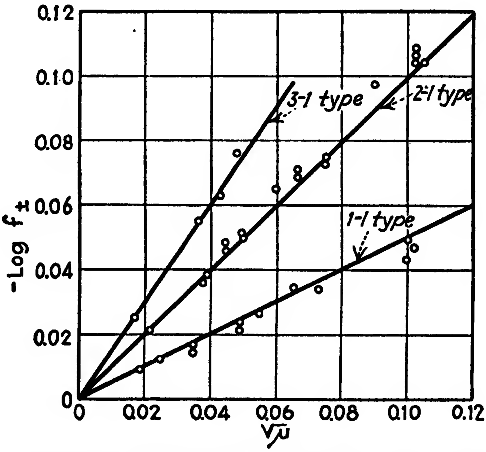

FIG. 3.—The activity coefficient as a function of the ionic strength.

nitrate, barium chloride, etc. As the solution is diluted, the latter values come into agreement with the theoretical, but the former do not show agreement even at the lowest dilution. This discrepancy between theory and experiment is well illustrated by the activity coefficients of zinc sulfate obtained by Cowperthwaite and La Mer† from e.m.f. measurements. In Table III these data are listed as well as the theoretically calculated values, and it can be seen that no agreement at all exists. Later we shall see how the mathematical treatment may be modified to agree with experiment.

Before turning to a consideration of nonaqueous solutions we may conclude that for aqueous solutions the activity coefficient

* LA MER, KING, and MASON, *J. Am. Chem. Soc.*, **49**, 363, 410 (1927); see also LA MER, COOK, and GOLDMAN, *ibid.*, **51**, 2622, 2632 (1929).

† COWPERTHWAITE and LA MER, *J. Am. Chem. Soc.*, **53**, 4333 (1931).

equation of Debye and Hückel is valid in a quantitative way only for very dilute solutions of uniunivalent salts.

In the Debye and Hückel theory, nonaqueous solutions should only differ from aqueous solutions to the extent that the dielectric constant of the solvent differs from that of water. A decrease in the dielectric constant increases the electrical forces between the ions so that we should expect the interionic attractions to be greater in nonaqueous solutions. This is due to the fact that practically all nonaqueous solvents have a lower dielectric constant than water. In our study of aqueous solutions we found that the variables which increase the electrical forces such as

TABLE III.—ACTIVITY COEFFICIENTS OF $ZnSO_4$ AT 25°C. SOLVENT: WATER

m	$\gamma_{\pm}(obs.)$	$\gamma_{\pm}(calc.)$
0.0005	0.780	0.863
0.001	0.700	0.812
0.002	0.608	0.745
0.005	0.477	0.627
0.01	0.387	0.517

increase of valence or increase of concentration result in failure of the Debye and Hückel equation to agree with the data. Since the electrical forces are also increased by a diminution in the dielectric constant, we should expect the Debye theory to be less valid in nonaqueous solutions than it is in aqueous. In other words, the behavior of a uniunivalent salt in a nonaqueous solvent like alcohol would be comparable to the behavior of a unibivalent salt in water, let us say. Williams, and Hansen and Williams* have investigated the solubility of some difficultly soluble salts in methyl alcohol solutions of various salts and in ethyl alcohol–water mixtures. A comparison of the theoretical ratio, $-(\ln f_{\pm})/\sqrt{\mu}$, with the experimentally found values for methyl alcohol at 20°C. is given in Table IV. In no case can it be said that the theory is verified quantitatively except, perhaps, in a few cases; here the agreement may be fortuitous. For the 2-1 and 3-1 valence-type saturating salts, the observed slopes

* J. W. WILLIAMS, *J. Am. Chem. Soc.*, **51**, 1112 (1929); HANSEN and WILLIAMS, *ibid.*, **52**, 2759 (1930); WILLIAMS, *Chem. Rev.*, **8**, 303 (1931).

TABLE IV.—COMPARISON OF EXPERIMENTAL AND THEORETICAL SLOPES, I.E., $-\ln f_{\pm}/\sqrt{\mu}$, FOR METHYL ALCOHOL SOLUTIONS AT 20°C.

Saturating salt	Valence type	Solvent salt	Slope obs.	Slope calcd.
Croceo chloride	1-1	$C_6H_5SO_3Na$	1.7	2.0
Croceo chloride	1-1	KSCN	1.7	2.0
Croceo chloride	1-1	$Ba(ClO_3)_2$	2.5	2.0
Croceo chloride	1-1	$(C_6H_5COO)_2Sr$	1.7	2.0
Chloropentammine cobalt nitrate	2-1	KSCN	4.0	4.0
Chloropentammine cobalt nitrate	2-1	$Ba(ClO_3)_2$	8.0	4.0
Xantho chloride	2-1	KSCN	4.0	4.0
Xantho chloride	2-1	$Ba(ClO_3)_2$	6.0	4.0
Xantho chloride	2-1	$(C_6H_5COO)_2Sr$	6.0	4.0
Luteo bromide	3-1	KSCN	11.5	6.0

differ from the theoretical by as much as 100 per cent in some instances. However, there can be no doubt that the theory predicts qualitatively the effect of the change in the dielectric constant. This is well illustrated by the interesting data of Hansen and Williams who studied the activity coefficients in ethyl alcohol–water mixtures at 25°C. In these experiments the dielectric constant could be varied at will between 78.8 and 30 merely by changing the ratio of ethyl alcohol to water. Sodium chloride was the solvent salt in all the experiments. The data, given in Table V, prove that as the dielectric constant is lowered the slope increases as predicted by Eq. (43), but that quantitative agreement which is excellent in water does not exist in the solutions of low dielectric constant. It is possible that the formation of undissociated molecules or of triple ions makes the observed slope greater than the calculated slope.

In conclusion we can say that the simple, unmodified theory of Debye and Hückel is quantitatively valid only in the case of uniunivalent salts in dilute solutions of solvents having a high dielectric constant. Expressed in other words we can say that the Debye and Hückel equations are valid when the electric forces between the ions are small.*

* See also J. N. BRØNSTED, AGNES DELBANCO, and KIRSTEN VOLQVARTZ, *Z. physik. Chem.*, A **162**, 128 (1932).

TABLE V.—COMPARISON OF EXPERIMENTAL AND THEORETICAL SLOPES $(-(\ln f_{\pm})/\sqrt{\mu})$ FOR ETHYL ALCOHOL–WATER MIXTURES AT 25°C.

Solvent mole fraction H_2O	Dielectric constant	Slope obs.	Slope calc.
1-1 Type salt. Croceo tetranitrodiamminocobaltiate			
1.00	78.8	0.50	0.50
0.80	54.0	0.89	0.89
0.60	41.4	1.31	1.32
0.40	33.8	1.90	1.80
1-2 Type salt. Crocco sulfate			
1.00	78.8	1.10	1.08
0.80	54.0	1.74	1.76
0.60	41.4	2.74	2.65
3-1 Type salt. Luteo iodate			
1.00	78.8	1.52	1.51
0.80	54.0	4.0	2.65
0.60	41.4	6.1	3.98

Extensions and Modifications of the Debye Theory.—The original mathematical treatment of Debye and Hückel may be modified in two general ways; in the first place the mathematics can be made more rigorous in a number of ways such as by considering more than the first term in the series expansion of Eq. (26); in the second place several of the physical assumptions made in the derivation may be avoided or made more reasonable; for example, the ion may be regarded as having a finite size instead of being considered merely as a point charge.

Debye and Hückel* in their original paper derived an equation for the activity coefficient in which the "ion size" **a** was introduced into the theory. The quantity **a** measures the distance of closest approach of another positive or negative ion; if the positive and negative ions are of the same size, **a** would be equal to the diameter of the ion. Since very little is known concerning the sizes of ions in solutions, the introduction of **a** into the theory

* DEBYE and HÜCKEL, *Physik. Z.*, **24**, 185 (1923).

is equivalent to introducing a constant which may be varied at will to fit the data. Debye and Hückel found that taking into account the finite size of ions modifies the final equation for the logarithm of the activity coefficient only by the factor $\frac{1}{1 + \mathbf{a}\kappa}$. The equation for the ionic activity coefficient is, therefore, from Eq. (40*b*)

$$\ln f_i = -\frac{z_i^2 \epsilon^2}{2DkT} \frac{\kappa}{(1 + \mathbf{a}\kappa)}. \tag{46}$$

In the derivation of Eq. (46) it is necessary to replace $\mathbf{a}_i$ characteristic of a single ion kind by the value $\mathbf{a}$ which is an "average" diameter, although it is not clear just what sort of an average value it is. The activity coefficient of a uniunivalent salt as a whole in water at 25°C. is

$$\log f_\pm = -\frac{0.506\sqrt{c}}{1 + 0.3 \times 10^8 \mathbf{a}\sqrt{c}}. \tag{47}$$

Putting this equation into the form of an equation of a straight line, we obtain

$$-\frac{0.506\sqrt{c}}{\log f_\pm} = 0.3 \times 10^8 \mathbf{a}\sqrt{c} + 1. \tag{48}$$

By plotting $\frac{\sqrt{c}}{\log f_\pm}$ against $\sqrt{c}$, a straight line should result if Eq. (48) is valid. La Mer and Goldman* list some values of $-\log \mathrm{f}_\pm$ and $\sqrt{\mu}$ (the square root of the ionic strength may be plotted instead of the square root of the concentration; this involves merely an alteration in the values of the numerical constants) which are particularly convenient to test Eq. (48). The values are for the activity coefficient of lanthanum iodate in potassium chloride aqueous solutions at 25°C. At very low concentrations the data are in harmony with the Debye and Hückel limiting equation (43), as might be expected inasmuch as the factor $1/(1 + \mathbf{a}\kappa)$ becomes equal to unity as the concentration approaches zero. But at higher concentrations the experimental activity coefficient deviates from the theoretical prediction of the limiting equation as is evident from Table VI; *i.e.*, the

*La Mer, and Goldman, *J. Am. Chem. Soc.*, **51**, 2632 (1929).

activity coefficient does not diminish with increase of concentration as rapidly as the Debye theory predicts.

TABLE VI.—LANTHANUM IODATE DISSOLVED IN POTASSIUM CHLORIDE
SOLVENT: WATER AT 25°C.

μ	$\sqrt{\mu}$	$-\log f_{\pm}$, obs.	$-\log f_{\pm}$, calcd. by Eq. (43)	$\frac{-\sqrt{\mu}}{\log f_{\pm}}$
0.006467	0.08042	0.1203	0.1218	0.6685
0.01085	0.1042	0.1503	0.1578	0.6933
0.01619	0.1272	0.1751	0.1928	0.7264
0.05800	0.2408	0.2862	0.3649	0.8414
0.1094	0.3308	0.3532	0.5011	0.9366
0.2113	0.4597	0.4349	0.6964	1.0570
0.5154	0.7179	0.5653	1.088	1.2699
1.021	1.010	0.6414	1.531	1.5746

A test of Eq. (48) is made in Fig. (4), and it can be seen that the data agree fairly well with this new function up to a value of

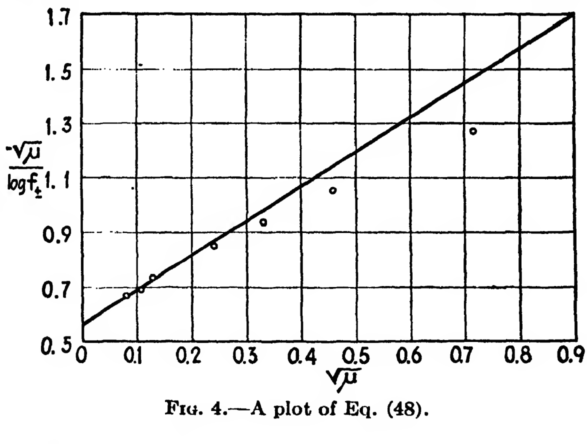

FIG. 4.—A plot of Eq. (48).

the ionic strength equal to 0.1, but above this concentration the equation fails to agree with the data. Apparently the introduction of the average ion size improves the theoretical equation: however, it is not sufficient for very concentrated solutions. Falkenhagen* has listed some values of the a constant which are interesting to study. These are given in Table VII. The values

* H. FALKENHAGEN, "Elektrolyte," pp. 255, 256, S. Hirzel, Leipzig, 1932.

are of the right order of magnitude but they have the peculiar property of decreasing with increasing atomic weight. One would expect that the ion size would increase as the atom gets heavier; the fact that the size decreases on going from sodium to potassium chloride is explained on the assumption that sodium

TABLE VII.—THE **a** CONSTANT OF EQUATION (48)

Salt	**a**, cm.	Distance between atoms in crystals
NaCl	4.02×10^{-8}	2.82×10^{-8}
KCl	3.76×10^{-8}	3.14×10^{-8}
K_2SO_4	2.69×10^{-8}	
$La(NO_3)_3$	4.97×10^{-8}	
$MgSO_4$	3.35×10^{-8}	
KNO_3	0.43×10^{-8}	

chloride is hydrated. The **a** value for potassium chloride is almost exactly what one would expect, but the **a** value for potassium nitrate is impossibly small. In many other cases it is necessary to select small or even negative values of **a**; hence this constant cannot be given any exact physical significance.

Gronwall, La Mer, and Sandved* have made an important contribution to the Debye theory by taking into consideration additional higher terms in the series expansion of Eq. (26). They also allow for a finite size of the ions and in so doing they succeed in circumventing the difficulty inherent in the introduction of very small or negative values of the **a** constant. Their equation for the activity coefficient of a "symmetrical" salt, *i.e.*, a salt with ions of equal valence is

$$\ln f_{\pm} = -\frac{\epsilon^2 z^2}{2kTD}\frac{\kappa}{(1 + \mathbf{a}\kappa)}$$
$$+ \sum_{m=1}^{\infty}\left(\frac{\epsilon^2 z^2}{kTD\mathbf{a}}\right)^{2m+1}\left[\frac{1}{2}X_{2m+1}(\mathbf{a}\kappa) - 2mY_{2m+1}(\mathbf{a}\kappa)\right]. \quad (49)\dagger$$

The first term of this equation is the same as the Debye and

* GRONWALL, LA MER, and SANDVED, *Physik. Z.*, **29**, 358 (1928).

† La Mer, Gronwall, and Greiff, *J. Phys. Chem.*, **35**, 2245 (1931), have extended this equation to salts of unsymmetrical valence type.

Hückel equation. The second term includes the functions $X(\mathbf{a}\kappa)$ and $Y(\mathbf{a}\kappa)$, the values of which have been calculated by Gronwall, La Mer, and Sandved, and are given in lengthy tables in their original paper. To use this equation it is first necessary to assume a value for **a**; then the corresponding values of the functions $Y(\mathbf{a}\kappa)$ and $X(\mathbf{a}\kappa)$ can be looked up in the tables and the value of $-\log f_{\pm}$ calculated. If the calculated value does not agree with the data, a new value of **a** is chosen and the calculation repeated. After a number of calculations, the value of **a** that best agrees with the data is finally chosen. Cowperthwaite and La Mer* have determined the activity coefficient of zinc sulfate in very dilute aqueous solutions and have interpreted their results quite successfully in the light of Eq. (49). Their values at 25°C. are given in Table VIII. (Compare Table III.)

TABLE VIII

c	**a** Debye and Hückel, Å.	**a** G., La M., and S., Å.	$f_{\pm}$, obs.	$f_{\pm}$, calcd. (Eq. 49)
0.0005	−11.01	3.64	0.780	0.780
0.001	− 8.22	3.63	0.700	0.701
0.002	− 5.53	3.65	0.608	0.608
0.005	− 2.33	3.64	0.477	0.478
0.01	− 0.31	3.62	0.387	0.386

The **a** values necessary to assume in the Debye and Hückel equation to make this equation agree with the data are given in column two, and it should be noticed that these values are negative and vary greatly with the concentration. The **a** values necessary to make the Gronwall, La Mer, and Sandved equation agree with the data are given in column three; these **a** values are physically reasonable and remain practically constant as the concentration is increased. In column four the experimentally determined activity coefficients are listed, and in column five are the activity coefficients calculated by Eq. (49) using the same **a** value, 3.64×10^{-8} cm., for all concentrations. This agreement is almost perfect.

* I. A. Cowperthwaite and V. K. La Mer, *J. Am. Chem. Soc.*, **53**, 4333 (1931).

The objection to the Gronwall, La Mer, and Sandved extension of the Debye theory is that it is subject to the same criticisms that the Debye theory is subject to. For example, it assumes the validity of Coulomb's law, the validity of the assumption of complete dissociation and the validity of the use of the Boltzmann equation. However, it is a decided improvement over the simple limiting law, and in the region of dilute solutions, it must be regarded as being the best solution of the activity coefficient problem that has yet been offered.*

Bjerrum has suggested that the difficulty of negative ions sizes can be overcome by the assumption of "ion association" in the case of ions having small radii, ion association for which the mass action law is valid. His theory has already been discussed in Chaps. II and V and in the hands of Fuoss and Kraus seems to be applicable in the case of solutions of low dielectric constant to the interpretation of the electrical conductance. Falkenhagen† points out that ionic diameters calculated from the theory of Gronwall, La Mer, and Sandved and from Bjerrum's‡ theory agree fairly well with each other.

Hückel has extended Eq. (47) up to high concentrations by introducing a term proportional to the concentration. This term is based on a linear decrease in the dielectric constant of the system with increase of concentration. His equation is

$$\ln f_{\pm} = \frac{-z_{+}z_{-}\epsilon^2}{2DkT}\frac{\kappa}{(1 + \mathrm{a}\kappa)} + B(c) \tag{50}$$

where B is a constant chosen to fit the data. Hückel's equation

* Cowperthwaite, La Mer, and Barksdale, *J. Am. Chem. Soc.*, **56**, 544 (1934), find that in the case of thallous chloride solutions an application of the Gronwall, La Mer, and Sandved extension of the Debye theory yields values of a for thallous chloride equal to 0.93 Å. which is physically too small since x-ray crystal-structure measurements show that 3.3 Å. is the distance of closest approach of the ions in the crystal lattice. They find, however, that if a partial dissociation of thallous chloride occurs having a dissociation constant 0.31, the Gronwall, La Mer, and Sandved treatment is applicable for values of a equal to 3.

† H. Falkenhagen, "Elektrolyte," p. 265, S. Hirzel, Leipzig, 1932.

‡ Bjerrum, *Det. Kgl. Danske Vidensk. Selskab. Math.-Fysik*, **7**, No. 9 (1926). See also W. Orthmann, *Erg. d. exakten Naturwissensch.* **6**, 161 (1926).

has found extensive application in the work of many people such as Harned, Scatchard, and others. Scatchard* has made use of Eq. (50) in calculating theoretical values of the e.m.f. of the cell

Na, Hg (2-phase amalg.)	NaCl (in water and alcohol mixtures)	HgCl | Hg

as a function of the mole fraction of the alcohol at concentrations of sodium chloride such that Nf is always equal to unity. Values

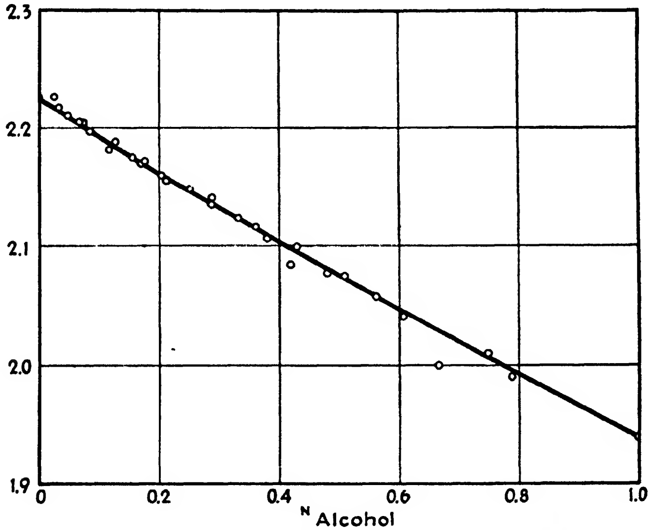

FIG. 5.—E.m.f. of alcohol-water sodium chloride cells.

of this e.m.f. which Scatchard denotes by the symbol E_N are also a function of the dielectric constant of the mixed alcohol-water solvent as well as being a function of the change in the dielectric constant due to the presence of the sodium chloride. In Fig. 5 the circles represent experimental values for E_N (calculated from solubility data) while the solid line illustrates the theoretical calculations of Scatchard. The agreement is excellent, but we must remember that Hückel's equation is in a sense empirical because it contains constants which must be chosen to fit the

* G. SCATCHARD, *J. Am. Chem. Soc.*, **47**, 2098 (1925); see also *ibid.*, **47**, 641, 3107 (1925); **48**, 2026 (1926); **49**, 217 (1927); *Chem. Rev.*, **3**, 383 (1927); *ibid.*, **13**, 7 (1933); H. S. HARNED and M. H. FLEYSHER, *J. Am. Chem. Soc.*, **47**, 82 (1925); **48**, 326 (1926), etc.

data. Scatchard* has discussed the work of Hückel, improving the theoretical calculations, and giving a new equation for the activity coefficient as a function among other things of the change in the dielectric constant with change of concentration, and of the sizes of the ions. But due to ignorance concerning the correct relation between dielectric constant and concentration, concerning the ion sizes, and concerning the magnitude of nonionic forces which Scatchard finds come into play, it is necessary to postpone describing Scatchard's equation [his equation No. (14)] until some of these uncertainties are cleared up.†

Exercises

1. Predict values for the activity coefficient of silver chloride in 0.1, 0.5, 1.0, and 4.0 N sodium chloride.

2. By means of the data of Table II, Chap. XVII, test graphically Bjerrum's equation (XVII-1) and compare it with Debye's equation (45).

3. When the point p lies outside of the sphere of Fig. 2, the potential at the point p is given by the equation

$$\psi = \frac{4}{3}\pi\frac{a^3}{r}\Pi.$$

Prove the Laplacian equation, $\Delta\psi = 0$.

4. Prove that $\psi = \frac{e^{-\kappa r}}{r}$ is a solution of the equation $\Delta\psi - \kappa^2\psi = 0$.

5. Amylamine has a dielectric constant of 4.5. Calculate the constant of Eq. (43) for this solvent at 25°C. Compare it with the corresponding value for water.

* G. Scatchard, *Physik. Z.*, **33**, 22 (1932); E. Hückel, *Physik. Z.* **26**, 93 (1925).

† See G. S. Hartley, *Trans. Faraday Soc.*, **31**, 31 (1935), for an illuminating discussion of the application of the Debye-Hückel theory to colloidal electrolytes. The latter substances may be treated as highly unsymmetrical salts (20-1 type, for example), and for this reason many of the assumptions which are valid for uniunivalent salts no longer hold. Hartley finds, however, as a result of his study of the problem that the interionic attraction effects are less than would be predicted by an unmodified application of the Debye theory. Hartley also discusses the inconsistencies inherent in the Boltzmann equation and the breakdown of the ionic-strength principle as the electrolytes become more and more unsymmetrical.

This volume of the Faraday Society Transactions contains many interesting applications of electrochemistry to the problems of colloidal electrolytes.

CHAPTER XIX

CONCENTRATION CELLS WITH LIQUID JUNCTIONS

Introduction.—Hitherto in this book we have considered solely e.m.f. cells in which we have compared two different electrodes with each other; we have not mentioned anything about cells in which the e.m.f. has been measured between like electrodes. If we have two similar electrodes such as two hydrogen electrodes or two calomel electrodes or two sodium amalgam electrodes and dip the two electrodes both into the same solution, it is obvious that the e.m.f. developed by the cell will be zero, because

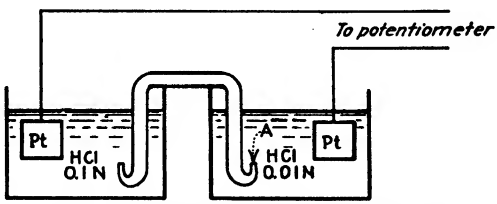

FIG. 1.—A hydrogen ion concentration cell.

both electrodes develop the same but oppositely directed potential. To obtain a measurable e.m.f. it is essential that the two electrodes be immersed into two different solutions, and that these two solutions be connected electrically by means of some sort of a solution junction. If the two solutions are connected by other metallic electrodes, the cell becomes an e.m.f. cell without a liquid junction, the type already treated in Chap. XVI. An example of the simplest type of a cell with a liquid junction is given in Fig. 1, which illustrates schematically a hydrogen ion concentration cell. The two platinum electrodes are immersed in two hydrochloric acid solutions of different concentrations and because of the difference in hydrogen ion concentration, there will be a measurable difference in e.m.f. for the cell as a whole. One would immediately think that from the measured e.m.f. it would be possible to calculate the difference in the activity

coefficient of the *hydrogen ion* in the two solutions, but this is not possible because of the potential that exists at the liquid junction between the concentrated and dilute solutions at point A of Fig. 1. The liquid junction potential at A depends upon the activity coefficients of both the hydrogen and chloride ions, and although the cell is called a hydrogen ion concentration cell, the total e.m.f. really is a function of the hydrochloric acid as a whole, as will be shown later. In concluding these introductory remarks, it can be stated that there is no experimental cell in which the ionic activity coefficient can be determined unambiguously. There are cells, to be described later, in which a very

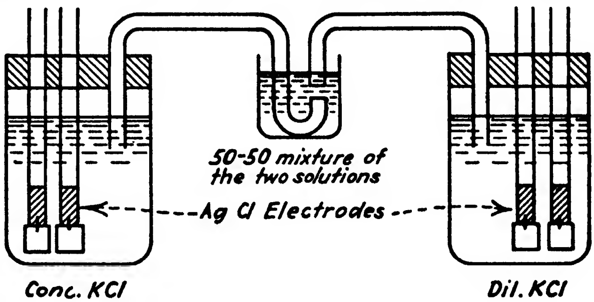

FIG. 2.—A chloride ion concentration cell with liquid junction.

close approximation to the correct change in the ionic activity coefficient can be obtained, however.

Types of Liquid-junction Cells.—A rather crude type of liquid-junction cell is illustrated in Fig. 2. This cell does not allow the boundary between the concentrated and dilute solutions to be formed in any definite manner; *i.e.*, it is impossible to say in what way the concentration varies between the dilute and concentrated solutions. However, if the two solutions are composed of the same solvent plus the same salt as in Fig. 2, it does not matter how the boundary is formed (as will be explained later, theoretically). MacInnes and Parker* used with success a cell similar to the one pictured in Fig. 2, although they found it necessary to renew the liquid junction just before making the measurement as the e.m.f. varied slightly with time.

Another possible type of liquid-junction cell permits the boundary to be formed in the narrow channels between a glass

* MACINNES and PARKER, *J. Am. Chem. Soc.*, **37**, 1445 (1915).

stopper and its sheath, Fig. 3.* The glass-stopper type of liquid-junction cell has the advantage that it apparently allows the two solutions to diffuse together rather than to mix mechanically as in the dipping type of Fig. 2. On the other hand, the electrical resistance around the glass stopper is comparatively large, and as a consequence the simple galvanometer cannot be used to measure the potential. The necessity of using an electrometer, vacuum-tube potentiometer, or ballistic galvanometer with condenser attachment to measure the potential is a disadvantage. Furthermore, Larsen† has demonstrated that the glass stopper type of cell fails to give a reproducible e.m.f. if the liquid-junction potential amounts to 8 mv. or more. To overcome this difficulty Lamb and Larsen‡ invented the flowing type of liquid-junction cell, in which the contact between the two solutions is continually renewed by allowing the solutions to flow constantly together. Such a cell is pictured in Fig. 4, where A is the point at which the denser solution comes in contact with the less dense solution. The reservoirs R and R' provide an excess amount of the two solutions which are allowed to flow slowly through the glass tubes to come to temperature equilibrium with the thermostat liquid before meeting at A. The rate of flow is roughly fifteen drops a minute. The potential is remarkably constant and reproducible as long as the flow continues.

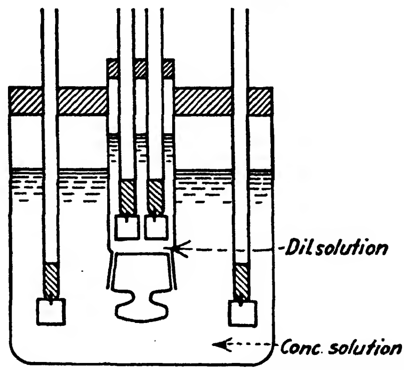

FIG. 3.—Glass-stopper type of liquid-junction cell.

A fourth method of forming the liquid junction between two solutions consists in artificially mixing the two solutions to form a series of solutions of different concentration which when joined together in a regular fashion are used as the bridge solution

* See GRINNELL JONES and M. L. HARTMANN, *J. Am. Chem. Soc.*, **37**, 752 (1915).

† LARSEN, Dissertation, Harvard, 1919.

‡ LAMB and LARSEN, *J. Am. Chem. Soc.*, **42**, 229 (1920); see also G. SCATCHARD, *ibid*, **47**, 696 (1925).

between the two electrode cells. Such a junction is called a "continuous-mixture junction," and should be of such a nature that the solution at any point in the junction can be formed by mixing the two end solutions together in the correct ratio. The flowing junction is considered to be a "continuous-mixture" type, because diffusion is a relatively slow process, and it is thought that the two solutions do not have time enough to diffuse together when they are brought in contact. The solutions must mix mechanically and not by diffusion; hence the flowing junction is a continuous-mixture junction.

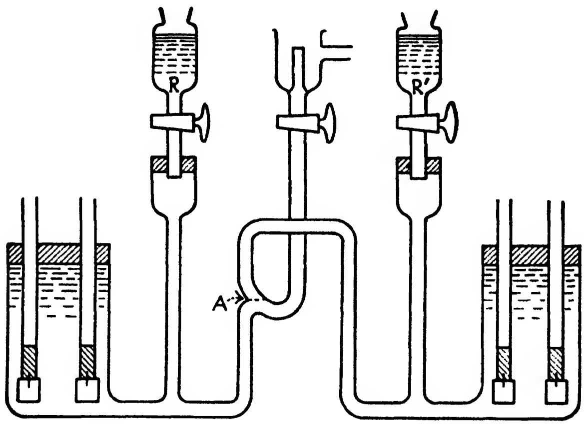

FIG. 4.—The flowing junction e.m.f. cell.

A liquid junction may be formed by merely bringing the two end solutions together with as sharp a boundary as possible and then allowing the two solutions to diffuse freely together. To obtain reproducible results with this type of junction it is advisable that the boundary be formed within a narrow tube so that the diffusion which takes place will be "cylindrically symmetrical." In the words of Guggenheim* a cylindrical symmetrical junction is one where "the gradients of the concentrations and of the electrical potential are throughout parallel to a fixed straight line." The ground-glass-stopper type of liquid junction seems to be of this type.

* E. A. GUGGENHEIM, *J. Am. Chem. Soc.*, **52**, 1315 (1930).

For certain theoretical reasons a "constrained-diffusion" junction is of interest, and may be prepared by allowing the two end solutions to diffuse together across a membrane, the surfaces of which are washed with the end solutions so that the diffusion layer always has the same thickness. A constrained-diffusion junction might also be formed by allowing the two solutions to diffuse together in a sintered glass mat. In this case the diffusion layer would be as thick as the mat. In the free-diffusion type, the thickness of the boundary layer is continually increasing.

Finally the two end solutions may be brought into electrical connection by connecting them together by the so-called "salt bridge." The salt bridge attempts to eliminate the liquid-junction potential by using a concentrated potassium chloride solution, the reason for this being that the net liquid junction potential across the two junctions, first solution ‖ salt bridge, and second solution ‖ salt bridge, decreases with rise of salt-bridge concentration and with decrease of the difference between the mobility of the positive and negative ions. The theoretical reasons for believing this last statement will be given shortly. The liquid junction used most frequently in laboratory experiments is the salt-bridge type.

Theory of Cells Composed of One Electrolyte.—Let us imagine that we have two hydrochloric acid solutions of concentrations c'(dilute) and c''(concentrated) and let us imagine that we set up a liquid-junction cell according to any of the above-mentioned types. For electrodes we can use either silver-silver chloride electrodes or hydrogen electrodes; let us choose the silver-silver chloride electrodes. At the first moment that solutions c' and c'' are brought into contact, hydrochloric acid will obviously tend to diffuse from the concentrated solution to the dilute, but the hydrogen ion will diffuse at first faster than the chloride ion due to its greater mobility in water. If more hydrogen ions than chloride ions depart from the concentrated solution, solution c'' will be left with excess chloride ions and will acquire a negative charge, while solution c' will gain excess hydrogen ions and will therefore become positive. The positive charge on the dilute solution will repel further migrations of hydrogen ions and will attract more chloride ions, so that when a steady state is attained, hydrogen ions and chloride ions will diffuse in equal numbers

from the concentrated to the dilute solution, but at the same time the dilute solution will be positive with respect to the concentrated solution.

The steady state is often loosely spoken of as a situation where equilibrium exists. In the sense in which equilibrium is used in thermodynamics we do not have equilibrium until diffusion has equalized the concentration of the two solutions. Then, of course, the liquid-junction potential becomes equal to zero. Statistically speaking, equilibrium is defined as the most probable configuration, any variation of which reduces the probability. In the case of liquid junctions the most probable configuration is that of uniform concentration throughout; this then is equilibrium. However, under the proper experimental conditions, the measured potential remains at a constant value; this is proof that a steady state has been attained.

Before deriving an equation for the potential at the liquid junction and for the e.m.f. of the cell as a whole, let us consider the question of reversibility of the process. It will be remembered that a reversible process is one in which any infinitesimal change in the external conditions will produce an infinitesimal change in the system and that the system may be brought back to its original condition merely by reversing the infinitesimal change in the external conditions. As the current is passed across a liquid junction, say between a sodium chloride solution and a potassium chloride solution, sodium ions will migrate into the potassium chloride solution, but on reversing the direction of the current, the transported sodium ions will not be returned to the sodium chloride solutions; potassium ions will be transported. Hence this process is essentially irreversible unless the two solutions differ in composition by only an infinitesimal amount. However, in the case of the liquid junction between two solutions formed of the same electrolyte, such as the two hydrochloric acid solutions, the migration of the ions is reversible irrespective of the nature of the boundary. Because of this we can solve the problem as Nernst did by a straightforward application of thermodynamics without the introduction of any assumptions. It also turns out that the resulting e.m.f. of the cell is independent of the manner in which the boundary is formed; hence, in this simple case of the same solute in the two solutions

we can use any type of a liquid junction (except the salt-bridge type) that we prefer.

Figure 5 is a schematic representation of a hydrochloric acid concentration cell, the liquid junction being at A and the electrodes being of the silver-silver chloride type. Let c' and c'' differ by an infinitesimal amount, and let the solutions be of such volume that the addition or subtraction of a mole of hydrogen chloride does not change the concentration. The cell of Fig. 5 if written down is

$$\mathrm{Ag}\,|\,\mathrm{AgCl}\left|\begin{matrix}\mathrm{HCl}\\(c+dc)\end{matrix}\right\|\begin{matrix}\mathrm{HCl}\\(c)\end{matrix}\left|\,\mathrm{AgCl}\,|\,\mathrm{Ag}.\right. \qquad (A)$$

As before the cell is so written that positive electricity flows to the right, the right-hand electrode is positive and the liquid

FIG. 5.

junction between the two solutions is designated by double vertical lines. We know that the right-hand electrode is positive with respect to the left-hand electrode because there is less tendency for the chloride ions to discharge at this electrode due to the lower concentration of chloride ions in the right-hand solution. The e.m.f. of cell (A) as a whole is easily derived if one takes into consideration the various reactions that occur on the passage of the current.

Let one faraday of electricity flow through the cell. At the left-hand (negative) electrode the following reaction occurs:

$$\mathrm{Ag} + \mathrm{Cl}^-(c + dc) \rightarrow \mathrm{AgCl} + \epsilon^-$$

and the net change in chemical potential is

$$\Delta\mu_1 = \mu_{\mathrm{AgCl}} + \mu_{\epsilon^-} - \mu_{\mathrm{Ag}} - \mu_{\mathrm{Cl}^-(c+dc)}. \qquad (1)$$

At the right-hand electrode the opposite reaction occurs;

$$\mathrm{AgCl} + \epsilon^- \rightarrow \mathrm{Ag} + \mathrm{Cl}^-(c),$$

and

$$\Delta\mu_2 = \mu_{\mathrm{Ag}} + \mu_{\mathrm{Cl}^-(c)} - \mu_{\mathrm{AgCl}} - \mu_{\epsilon^-}. \qquad (2)$$

At the liquid junction the current is carried partly by the hydrogen ion and partly by the chloride ion; considering the hydrogen ion, we have the reaction,

$$t_{H^+}H^+(c + dc) \rightarrow t_{H^+}H^+(c)$$

and a change in chemical potential

$$\Delta\mu_3 = -t_{H^+}[\mu_{H^+(c+dc)} - \mu_{H^+(c)}], \tag{3}$$

where t is the transference number (see Chap. IX). The chloride ion moves in the opposite direction to the hydrogen ion, the equations for its transfer are

$$t_{Cl^-}Cl^-(c) \rightarrow t_{Cl^-}Cl^-(c + dc),$$

and

$$\Delta\mu_4 = t_{Cl^-}(\mu_{Cl^-(c+dc)} - \mu_{Cl^-(c)}). \tag{4}$$

The net change in chemical potential for the cell as a whole is the sum of Eqs. (1), (2), (3), and (4) or

$$\Delta\mu = (t_{Cl^-} - 1)(\mu_{Cl^-(c+dc)} - \mu_{Cl^-(c)}) - t_{H^+}(\mu_{H^+(c+dc)} - \mu_{H^+(c)}). \tag{5}$$

But $t_{Cl^-} - 1$ is equal to $-t_{H^+}$ by Eq. (X-3), and since $\mu_{c+dc} - \mu_c$ is an infinitesimal increment, we can write Eq. (5)

$$d\mu = -t_{H^+}(d\mu_{Cl^-} + d\mu_{H^+}). \tag{6}$$

Introducing the e.m.f. and replacing the chemical potential o the chloride and hydrogen ions by the values as given in the equation,

$$\mu_i = \mu_i^\circ + RT \ln c_i \cdot \mathbf{f}_i, \tag{7}$$

or

$$d\mu_i = RT\, d \ln c_i \cdot \mathbf{f}_i, \tag{8}$$

we obtain

$$dE_t = 2t_{H^+}\frac{RT}{F}d \ln c_{HCl} \cdot \mathbf{f}_{\pm HCl}. \tag{9}$$

Calculation of the Transference Number from E.M.F. Measurements.—Before attempting to derive an equation which will give us the potential at the liquid junction, let us see what quantities of interest may be calculated from the e.m.f. E_t of the cell (A) as a whole. In Chap. IX it was mentioned that the transference number could be measured by employing suitable galvanic cells. If we measure the e.m.f. of cells of the type (B),

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{HCl}(c + dc) \mid \mathrm{H_2, Pt} - \mathrm{Pt, H_2} \mid \mathrm{HCl}(c) \mid \mathrm{AgCl} \mid \mathrm{Ag}, \tag{B}$$

we can calculate the transference number by combining e.m.f. values of (B) with e.m.f. values of (A) since the e.m.f. of cell (B) is given by the equation

$$dE = 2\frac{RT}{F}d \ln c_{\mathrm{HCl}} \cdot \mathbf{f}_{\pm\mathrm{HCl}}, \tag{10}$$

and since Eq. (9) divided by Eq. (10) gives the equation

$$\frac{dE_t}{dE} = t_{\mathrm{H^+}}. \tag{11}$$

In Eq. (11) E_t is the e.m.f. of the cell with liquid junction [cell (A)]. Equation (11) was first used in its correct differential form by MacInnes and Beattie.* We cannot integrate Eq. (11) to give

$$\frac{E_t}{E} = t_{\mathrm{H^+}} \tag{12}$$

since the transference number is not independent of the concentration. It should be noted that the transference number of Eq. (11) is the Hittorf transference number.

The easiest way of calculating the transference number from Eq. (11) is to plot values of E_t against values of E. (E_t and E must be measured between the same concentration intervals.) The slope of the curve dE_t/dE, gives immediately the value of the transference number at the particular concentration at which the slope is taken. This method is not accurate due to the difficulty in estimating slopes and has only been used in special cases where the authors were unable to work out a mathematical method of computing dE_t/dE. Jones and Dole† have described a precise, but laborious method of calculating the transference numbers from e.m.f. data. Their results for barium chloride solutions are given in Table I along with values determined by them by the analytical method described in Chap. IX. The agreement between the two sets of data is sufficiently good for the conclusion to be made that the e.m.f. method

* D. A. MacInnes and J. A. Beattie, *J. Am. Chem. Soc.*, **42**, 1117 (1920).

† Grinnell Jones and M. Dole, *J. Am. Chem. Soc.*, **51**, 1073 (1929).

gives the same results as the Hittorf analytical method. However, owing to the complicated calculations necessary and owing to the sensitivity of the results to the procedure used to calculate

TABLE I.—COMPARISON OF TRANSFERENCE NUMBERS AS MEASURED BY THE E.M.F. AND THE HITTORF METHOD. BARIUM CHLORIDE AQUEOUS SOLUTIONS AT 25°C.

c	t_+ from e.m.f. data	t_+ from analytical data
1.00	0.351	0.353
0.50	0.379	0.379
0.25	0.400	0.399
0.10	0.419	0.416
0.05	0.429	0.425
0.025	0.434	0.432
0.01	0.442	0.437

the e.m.f. transference numbers, the Hittorf analytical transference numbers are considered to be more reliable.*

The Potential at the Liquid Junction.—The potential at the liquid junction of cell (A) may be easily described mathematically by adding together Eqs. (3) and (4), the equations for the change in chemical potential for the reactions at the liquid junction, thus

$$d\mu_l = d\mu_3 + d\mu_4 = -t_{H^+}d\mu_{H^+} + t_{Cl^-}d\mu_{Cl^-} \tag{13}$$

or, on introducing the e.m.f., the concentration and the activity coefficients,

$$dE_l = t_{H^+}\frac{RT}{F}d\ln c_{H^+}\cdot \mathrm{f}_{H^+} - t_{Cl^-}\frac{RT}{F}d\ln c_{Cl^-}\cdot \mathrm{f}_{Cl^-}. \tag{14}$$

If we make the assumption that $\mathrm{f}_{Cl^-} = \mathrm{f}_{H^+} = \mathrm{f}_{\pm}$, we can simplify Eq. (14) to

$$dE_l = (t_{H^+} - t_{Cl^-})\frac{RT}{F}d\ln c\cdot \mathrm{f}_{\pm} \tag{15}$$

* Grinnell Jones and B. C. Bradshaw, *J. Am. Chem. Soc.*, **54**, 138 (1932), have shown that the method of Jones and Dole applied to lithium chloride data leads to different transference number values from the values previously obtained by MacInnes and Beattie, who used a different mathematical method of calculating the transference number from the e.m.f. data.

or

$$dE_l = \frac{u - v}{u + v}\frac{RT}{F}d \ln c \cdot \mathbf{f}_{\pm}, \tag{16}$$

since

$$t_+ = \frac{u}{u + v} \quad \text{and} \quad t_- = \frac{v}{u + v}.$$

In Eq. (16) u and v are the mobilities of the positive and negative ions, respectively (see Chap. V). Equation (16) tells us that if the mobilities of the positive and negative ions are equal, the liquid-junction potential E will be equal to zero. If $u > v$, the liquid-junction potential will be positive and will be added to the e.m.f. due to the two electrode reactions. If $v > u$, the liquid-junction potential will be negative, and will be subtracted from the e.m.f. due to the electrode reactions. In cell (A) the hydrogen ion has a much larger mobility than the chloride ion; hence the liquid-junction potential is positive and adds to the e.m.f. of the electrodes. In the case of the cell (C)

$$\text{Pt, } H_2 \mid HCl(c) \parallel HCl(c + dc) \mid H_2\text{, Pt} \tag{C}$$

the liquid-junction potential is given by the equation

$$dE_l = \frac{v - u}{v + u}\frac{RT}{F}d \ln c \cdot \mathbf{f}_{\pm}. \tag{17}$$

As before, $u > v$, but the liquid-junction potential is now negative and opposes the net e.m.f. of the electrodes. If the liquid-junction potential of cell (A) is positive, the liquid-junction potential of (C) must be negative since the concentrated and dilute solutions are reversed in the two cells. In the next section where more general equations for the liquid-junction potential are derived, we shall consider the more concentrated solution to be on the right as in cell (C). The more concentrated solution is designated by c'' and the more dilute by c'.

The General Equation for the Liquid-junction Potential.—Planck was the first to derive an equation for the liquid-junction potential which was applicable to solutions containing several species of ions. His solution was given only for ions of the same numerical valence, but Pleijel succeeded in generalizing Planck's*

* M. Planck, *Wied. Ann.*, **39**, 161 (1890); **40**, 561 (1890); Pleijel, *Z. physik. Chem.*, **72**, 1 (1910).

equation to include ions of several different valencies. Planck made the following assumptions:

1. That the solvent is the same throughout the junction.
2. That the mobility of the ions is constant throughout the junction.
3. That the laws of ideal solutions are obeyed.
4. That the junction between the two solutions is formed as follows: ions may diffuse freely between the parallel planes A and B but to the left of A and the right of B the concentrations of the original solutions remain unaltered.

Planck obtained the equation (for uni-univalent electrolytes)

$$E_l = \frac{RT}{F} \ln \xi \tag{18}$$

where ξ is defined by the equation

$$\frac{\sum\limits_{+} u_i'' c_i'' \xi - \sum\limits_{+} u_i' c_i'}{\sum\limits_{-} v_i'' c_i'' - \sum\limits_{-} v_i' c_i' \xi} = \frac{\ln \dfrac{\sum\limits_i c_i''}{\sum\limits_i c_i'} - \ln \xi}{\ln \dfrac{\sum\limits_i c_i''}{\sum\limits_i c_i'} + \ln \xi} \times \frac{\sum\limits_i c_i'' \xi - \sum\limits_i c_i'}{\sum\limits_i c_i'' - \sum\limits_i c_i' \xi}. \tag{19}$$

In Eq. (19) $\sum\limits_i$, $\sum\limits_-$ and $\sum\limits_+$ signify that the summation is to be taken over all ions, all negative ions and all positive ions, respectively. This transcendental equation becomes especially simple for certain cases. If both solutions are composed of solvent plus the same solute as in Fig. 2, Eq. (18) becomes

$$E_l = \frac{RT}{F} \frac{v - u}{v + u} \ln \frac{c''}{c'} \tag{20}$$

which is the integrated form of Eq. (17) assuming no change in activity coefficient in integrating. If both solutions have the same concentration of solute with one ion in common, for example, 0.1 N sodium chloride in junction with 0.1 N potassium chloride, Eq. (18) becomes

$$E_l = \frac{RT}{F} \ln \frac{v + u'}{v + u''}, \tag{21}$$

where u' and u'' refer to the mobilities of the positive ions on the left and right of the junction, respectively. If the negative ions, for example, have such a low mobility that they can be neglected in comparison with the positive ions, Eq. (18) reduces to

$$E_l = \frac{RT}{F} \ln \frac{\sum\limits_{+} u_i'c_i'}{\sum\limits_{+} u_i''c_i''}. \tag{22}$$

Henderson,* by assuming a "continuous-mixture boundary" in addition to the necessary assumptions concerning the constancy of the ionic mobilities and the validity of the gas laws, was able to derive a simpler equation than Planck's. Henderson's equation is only applicable to liquid junctions in which the solution at any point through the boundary can be formed by adding together definite quantities of the two end solutions. Such a junction is unstable because diffusion will occur and will change the concentration throughout the boundary from the value required by the assumption of continuous mixing. Henderson's equation which is generally applicable is

$$E_l = \frac{RT}{F} \frac{(\mathrm{U_{II}} - \mathrm{V_{II}}) - (\mathrm{U_I} - \mathrm{V_I})}{(\bar{\mathrm{U}}_{\mathrm{II}} + \bar{\mathrm{V}}_{\mathrm{II}}) - (\bar{\mathrm{U}}_{\mathrm{I}} + \bar{\mathrm{V}}_{\mathrm{I}})} \ln \frac{\bar{\mathrm{U}}_{\mathrm{I}} + \bar{\mathrm{V}}_{\mathrm{I}}}{\bar{\mathrm{U}}_{\mathrm{II}} + \bar{\mathrm{V}}_{\mathrm{II}}}. \tag{23}$$

In Eq. (23)

$$\begin{aligned} \bar{\mathrm{U}}_{\mathrm{II}} &= \sum_{+} u_i''z_ic_i'' & \qquad \bar{\mathrm{V}}_{\mathrm{II}} &= \sum_{-} v_i''z_ic_i'' \\ \bar{\mathrm{U}}_{\mathrm{I}} &= \sum_{+} u_i'z_ic_i' & \bar{\mathrm{V}}_{\mathrm{I}} &= \sum_{-} v_i'z_ic_i' \\ \mathrm{U_{II}} &= \sum_{+} u_i''c_i'' & \mathrm{V_{II}} &= \sum_{-} v_i''c_i'' \\ \mathrm{U_I} &= \sum_{+} u_i'c_i' & \mathrm{V_I} &= \sum_{-} v_i'c_i', \end{aligned}$$

where $\sum\limits_{+}$ and $\sum\limits_{-}$ mean the summation over all positive and negative ions, respectively. For the three simple cases mentioned above in which the Planck equation reduces to a simple expression Henderson's equation also reduces to exactly the same expression; hence we can conclude that in these three special cases it does

* HENDERSON, *Z. physik. Chem.*, **59**, 118 (1907); **63**, 325 (1908).

not matter how the junction is formed, the liquid-junction potential is always the same. Guggenheim* has compared experimental values of the e.m.f. of the cell

$$\mathrm{Hg} \mid \mathrm{HgCl} \mid 0.1\ N\ \mathrm{HCl} \underset{B}{\|} c\mathrm{KCl} \mid 0.1\ N\ \mathrm{KCl} \mid \mathrm{HgCl} \mid \mathrm{Hg} \quad (D)$$

when the junction B is formed by "free diffusion" and by "continuous mixing." He also measured some cells in which the junction was the "constrained-diffusion" type required by Planck's equation. No significant difference in the e.m.f. could be found between any of the different types of cells (see Fig. 6).

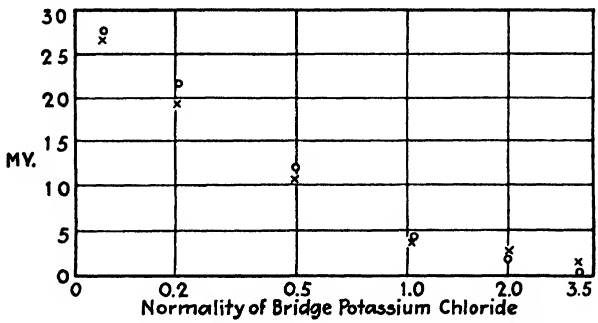

FIG. 6.—o, continuous-mixture layer; x, free diffusion.

In Fig. 6 the concentration of the bridge potassium chloride is plotted logarithmically for convenience, and it is interesting to note that as the concentration of the bridge solution increases the liquid-junction potential declines nearly to zero. This explains the previously mentioned fact that a saturated solution of potassium chloride is usually used as the bridge liquid. A study of Eq. (23) also proves that the liquid-junction potential becomes smaller the more equal are the mobilities of the positive and negative ions of the bridge solution; this is a second reason for using potassium chloride solutions.

Taylor† has extended Henderson's equation to allow a variation in ionic mobilities and to permit the use of variable activity coefficients. However, Guggenheim has questioned Taylor's assumptions underlying his mathematical treatment. Unfor-

* E. A. GUGGENHEIM, *J. Am. Chem. Soc.*, **52**, 1315 (1930).

† P. B. TAYLOR, *J. Phys. Chem.*, **31**, 1478 (1927).

tunately the mathematical difficulties in obtaining a general solution for the liquid-junction equation are very great.

Taylor was the first to point out that it is impossible to calculate *ionic* activity coefficients from the data because the e.m.f. of any cell that can be imagined is a function of the product of the activities of the positive and negative ions present and this product may never be resolved into the separate ionic activities. Guggenheim* states, "the electric potential difference between two points in different media can never be measured and has not yet been defined in terms of physical realities; it is therefore a conception which has no physical significance." Guggenheim means by the word "medium" a system in which the solvent is the same throughout and all the solute species behave independently. Different media are two solutions having different solvents, or two solutions having the same solvent but different concentrations of solute. In the chapter on Phase Boundary Potentials we shall make use again of this important concept of Guggenheim. In the meantime we may perhaps speak frequently of ionic activity coefficients or of ionic concentrations as measured by e.m.f. measurements. We do this as a matter of convenience, but the reader should always keep in mind that ionic activity coefficients and ionic concentrations cannot be measured unambiguously by e.m.f. measurements. However, in certain instances† it is possible to measure a change in ionic concentration rather accurately by e.m.f. measurements.

Exercises

1. Derive an equation similar to Eq. (9) for a barium chloride concentration cell using barium amalgam electrodes.
2. Derive Eq. (17).
3. Prove that both the Planck and Henderson equations reduce to Eq. (21) for the special case there under consideration.
4. If the e.m.f. of the following cell is known, demonstrate how it is possible to make an approximate calculation of the ionic product K_w for water (see Chap. XXI for a precise method of obtaining K_w from e.m.f. data).

$$\mathrm{Pt,\ H_2} \mid 0.1\ N\ \mathrm{NaOH} \left\| \begin{matrix}\mathrm{KCl} \\ \text{salt bridge}\end{matrix} \right\| 0.1\ N\ \mathrm{HCl} \mid \mathrm{H_2,\ Pt}$$

5. Describe the e.m.f. cell which would enable an approximate calculation to be made (in much the same way as the calculation of Exercise 4) of the solubility of silver chloride in water and outline the method of calculation.

* E. A. Guggenheim, *J. Phys. Chem.*, **33**, 842 (1929); **34**, 1540 (1930).

† In electrometric titrations, for example.

CHAPTER XX

HOMOGENEOUS IONIC EQUILIBRIA

I. THE MASS ACTION LAW

Introduction.—From conductance and e.m.f. data we can obtain considerable information concerning the behavior of acids, bases, and salts in solution. For example, we can measure the strength of acids and bases and we can determine the extent of hydrolysis of salts in aqueous solution. The dissociation constant of water, an exceedingly important quantity, may be calculated from data obtained by several different experiments. It is the purpose of this and following chapters to describe briefly the methods employed by electrochemists in the measurement of dissociation constants and other numerical quantities which are of interest.

Guldberg and Waage, in 1867, first formulated the *law of mass action* (abbreviated hereafter as L.M.A), the law which governs the position of chemical equilibrium in a reaction as a function of the proportions of reactants and products involved. Guldberg and Waage stated that the extent to which a reaction would go to completion depended upon the *active masses* of the reactants and products present in the reaction mixture when equilibrium was reached. The active masses of Guldberg and Waage were originally interpreted to be equivalent to the concentration (moles per liter of solution) of the substances present, but as will be emphasized below, we know now that activities, *i.e.*, concentrations multiplied by activity coefficients rather than concentrations are to be identified as the active masses of Guldberg and Waage.

The application of the L.M.A. to the reaction of dissociation is of particular interest to electrochemists. In fact, when Arrhenius* was first advancing his theory of dissociation, both van't Hoff and Ostwald suggested to him that if his theory was

* S. Arrhenius, *J. Am. Chem. Soc.*, **34**, 353 (1912).

true, the L.M.A. must necessarily be valid for the dissociation of all acids, bases, and salts. As has already been mentioned in Chaps. II and V, Ostwald followed up this suggestion and applied the L.M.A. to the reaction of dissociation, obtaining the "Ostwald dilution law."*

In this chapter however, we shall not consider the Ostwald dilution law again; we shall concern ourselves with the calculation of the dissociation constant K. In the case of any solute which on dissociation gives rise to the cation P and the anion N the equation for the dissociation is

$$PN \rightleftarrows P^+ + N^-, \tag{1}$$

and the L.M.A., as applied by Ostwald is,

$$K_c = \frac{c_p \cdot c_n}{c_{pn}}. \tag{2}$$

In Eq. (2) the concentrations are expressed in the units of moles per liter of solution and K_c is the dissociation constant when concentrations are used for the active masses of Guldberg and Waage. If we know the concentration of the two ions and of the undissociated molecule PN at any particular concentration, we can calculate the dissociation constant at that concentration. We can calculate K_c at another concentration by substituting values of c_p, c_n, and c_{pn} at this second concentration into Eq. (2). For the unmodified Arrhenius theory to be valid, values of K_c should be constant as the concentration is varied.

In order to test Eq. (2) it is necessary to know the concentrations of the various products and reactants of reaction (1). According to the simple Arrhenius theory, these values for the ions can be calculated by multiplying the conductance ratio

$$\frac{\Lambda}{\Lambda_0}$$

by the stoichiometrical concentration and for the undissociated molecule by multiplying $\left(1 - \frac{\Lambda}{\Lambda_0}\right)$ by the stoichiometrical concentration. Equation (2) may be written, therefore,

* W. Ostwald, *Z. physik. Chem.*, **2**, 36, 270 (1888).

$$K_c = \frac{(\Lambda/\Lambda_0)^2 c^2}{\left(1 - \frac{\Lambda}{\Lambda_0}\right)c} = \frac{\alpha^2 c}{1 - \alpha}, \tag{3}$$

where α is the degree of dissociation (see Chap. V). Some scientists have multiplied the conductance ratio by the viscosity ratio η/η_0, but there is considerable diversity of opinion concerning the viscosity correction; hence we shall omit that factor from Eq. (3).

It is an interesting historical fact that Arrhenius first tested Eq. (3) with acetic acid solution data. In the case of acetic acid, the L.M.A. gives rather good agreement, as has already been mentioned in Chap. II. In the next section we shall describe two modern methods for determining the dissociation constant of acetic acid with great accuracy. For strong electrolytes, such as potassium chloride, values of K_c calculated at various concentrations are not constant but vary by as much as two-hundred-fold. This is illustrated by the data of Table I quoted from Partington.* There is no indication that K_c is a constant in any concentration range.

TABLE I.—DISSOCIATION OF POTASSIUM CHLORIDE AT 18°C. ACCORDING TO THE ARRHENIUS THEORY

c	Λ	α	K_c
1	98.27	0.7565	2.350
0.1	112.03	0.8624	0.5405
0.01	122.43	0.9424	0.1542
0.001	127.34	0.9802	0.0485
0.0001	129.07	0.9936	0.0154

The Dissociation Constant of Acetic Acid.—According to modern theories of solution it is incorrect to calculate the degree of dissociation α from the conductance ratio, Λ/Λ_0, because the mobilities of the ions are not independent of the concentration as Arrhenius assumed. The mobilities decrease as the concentration decreases due to the electrical attractions between the ions. In calculating the dissociation constant K_c we should use, therefore, values of Λ_0 which have been corrected for the change of

* "A Treatise of Physical Chemistry," Vol. I, p. 557, 1st ed., D. Van Nostrand Company, New York, 1924.

ionic mobility. Davies* was the first to point this out. Sherrill and Noyes, and MacInnes† have also come to the same conclusion. In Chaps. V and VI the exact method used by MacInnes and Shedlovsky‡ in calculating α from their most recent data has been described in detail. From conductance data of hydrochloric acid, sodium acetate and sodium chloride, they were

TABLE II.—EQUIVALENT CONDUCTANCES AND DISSOCIATION CONSTANT VALUES OF ACETIC ACID AT 25°C.

Total concn. $c \times 10^3$	Ion concn. $c_i \times 10^4$	Λ_e	Λ	$K_c \times 10^5$	$K \times 10^5$
0.028014	0.15107	390.02	210.32	1.768	1.752
0.11135	0.36491	389.68	127.71	1.779	1.754
0.15321	0.44049	389.61	112.02	1.777	1.750
0.21844	0.54101	389.49	96.466	1.781	1.751
1.02831	1.2727	388.94	48.133	1.797	1.751
1.36340	1.4803	388.81	42.215	1.803	1.753
2.41400	2.0012	388.52	32.208	1.809	1.750
3.44065	2.4092	388.32	27.191	1.814	1.750
5.91153	3.1929	387.99	20.956	1.823	1.749
9.8421	4.1557	387.61	16.367	1.832	1.747
12.829	4.7591	387.41	14.371	1.834	1.743
20.000	5.975	387.05	11.563	1.840	1.738
50.000	9.524	386.19	7.356	1.849	1.721
52.303	9.7542	386.07	7.200	1.854	1.723
100.000	13.496	385.29	5.200	1.846	1.695
119.447	14.763	385.07	4.759	1.847	1.689
200.000	18.992	384.41	3.650	1.821	1.645
230.785	20.371	384.15	3.391	1.814	1.633

able to calculate the equivalent conductance of *completely dissociated* acetic acid at any desired ionic concentration. This value Λ_e, when divided into the observed equivalent conductance Λ, gave them the corrected value of α, *i.e.*,

$$\frac{\Lambda}{\Lambda_e} = \alpha. \tag{4}$$

* C. W. DAVIES, *J. Phys. Chem.*, **29**, 977 (1925).

† SHERRILL and NOYES, *J. Am. Chem. Soc.*, **48**, 1861 (1926); D. A. MACINNES, *J. Am. Chem. Soc.*, **48**, 2068 (1926).

‡ D. A. MACINNES and T. SHEDLOVSKY, *J. Am. Chem. Soc.*, **54**, 1429 (1932); see Brockman and Kilpatrick, *ibid.*, **56**, 1483 (1934), for a similar treatment of benzoic acid data.

MacInnes and Shedlovsky next calculated values of K_c according to Eq. (3) using values of α obtained through Eq. (4). Their results for Λ_e, Λ, and K_c are given in the third, fourth, and fifth columns of Table II. The dissociation constant for acetic acid calculated in this way is nearly constant over a wide range of concentrations. But there is a noticeable increase in its value to a maximum of 1.854 with increase of concentration. Further increase of concentration again lowers K_c, the variation of K_c with concentration being considerably greater than the experimental uncertainties.

A thermodynamic derivation of the L.M.A. from a consideration of the change in chemical potentials of the reactants and products during a reaction was given in Chap. XV. It was shown that for a nonideal solution one must include activity coefficients in the mass action equation. Equation (2) as written correctly [compare Eq. (XV-62)] is

$$K = \frac{N_p \cdot f_p \cdot N_n \cdot f_n}{N_{pn} \cdot f_{pn}}. \tag{5}$$

Concentrations are more frequently expressed in moles per liter of solution than in mole fractions; hence we shall actually make use of the mass action equation,

$$K = \frac{c_p \cdot c_n \cdot \mathbf{f}_p \cdot \mathbf{f}_n}{c_{pn} \cdot \mathbf{f}_{pn}} \tag{6}$$

rather than Eq. (5). In Eq. (6) c_{pn} and $\mathbf{f}_{pn}$ are the concentration and activity coefficients, respectively, of the undissociated molecules. It is reasonable to assume that the activity of the neutral undissociated molecule is not affected by the interionic attractions, so that in dilute solutions we may set $\mathbf{f}_{pn}$ equal to unity. If $\mathbf{f}_\pm$ represents the mean activity coefficient of the two ions $(+\sqrt{\mathbf{f}_p \cdot \mathbf{f}_n})$ K_c and K are related by the equation

$$K = K_c \cdot \mathbf{f}_\pm^2, \tag{7}$$

or

$$\log K = \log K_c + 2 \log \mathbf{f}_\pm. \tag{8}$$

It will be remembered that in Chap. XVIII the mean activity coefficient of an ion was shown, on the basis of the Debye and Hückel theory, to be given by the equation (for a uniunivalent salt dissolved in water at 25°C.)

$$\log f_{\pm} = -0.5065\sqrt{c_i}, \tag{9}$$

where c_i is the concentration of the ions. Substituting this value of $\log f_{\pm}$ into Eq. (8) we obtain

$$\log K = \log K_c - 1.013\sqrt{c_i}. \tag{10}$$

Equation (10) enables us to make a test of the Debye theory on the basis of the dissociation constants as calculated from conductance measurements. As already mentioned in Chap. XVIII, the results verify the theory within the experimental uncertainties. This can be readily seen from Fig. 1, where the

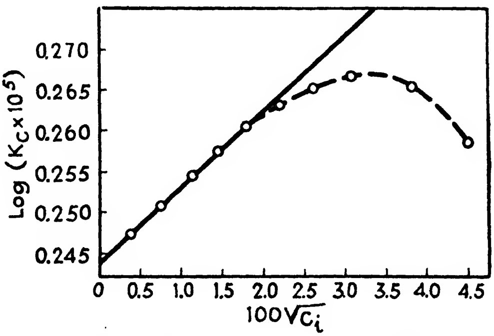

FIG. 1.—Log K_c for acetic acid as a function of the square root of the ionic concentration.

log of $K_c \times 10^5$ is plotted as a function of the square root of c_i. According to Eq. (10) the curve should be a straight line with intercept on the ordinate equal to log K. The lowest five points not only fall on a straight line, but the line has the theoretical slope, -1.013, within the experimental error. At higher concentrations the calculated values of $\log K_c$ go through a maximum as has already been mentioned. MacInnes and Shedlovsky attribute this variation in $\log K_c$ to the influence of undissociated acetic acid molecules on the medium (called by them the medium effect).

By applying the method of least squares to their data, MacInnes and Shedlovsky calculate the value of K_c at zero concentration, which is also the value of K, to be 1.753×10^{-5}. It might be pointed out here that the unmodified Arrhenius method of calculating the dissociation constant gave 1.84×10^{-5} according to the data of Kendall.* The difference between the values

* JAMES KENDALL, *J. Chem. Soc.*, **101**, 1275 (1912).

1.75×10^{-5} and 1.84×10^{-5}, while slight, is greater than the experimental error and proves that the Debye theory must be considered in computing the dissociation constants for weak electrolytes.

The validity of the MacInnes and Shedlovsky method of calculating the mass action constant may be tested by calculating K over a series of concentrations by means of Eq. (10); K so calculated should be a constant independent of the concentration if the Arrhenius theory is correct, if the Debye and Hückel theory is valid and if the neglect of the activity coefficient of the neutral molecules does not introduce too great an error. Values of K are given in the sixth column of Table II and it is readily seen that at the ten lowest concentrations, variations of K from the average are very small. Within this range of concentration, which corresponds to the *ionic* concentration limits 0.00001 to 0.0003 normal, both the Debye and Hückel and the Arrhenius theories as well as our assumptions seem to be valid.

The dissociation constants for weak acids and bases may also be determined by purely thermodynamical methods that involve neither conductance measurements nor assumptions as to liquid junction potentials. Following the method of Harned and Owen,* Harned and Ehlers† have determined the dissociation constant of acetic acid from 0° to 35°C. at intervals of 5°. The experimental procedure consisted in measurements of the e.m.f. of the cell

$$\mathrm{Pt, H_2 \mid HOAc}(m_1), \mathrm{NaOAc}(m_2), \mathrm{NaCl}(m_3) \mid \mathrm{AgCl} \mid \mathrm{Ag}, \qquad (A)$$

where HOAc and NaOAc represent acetic acid and sodium acetate, respectively. The concentration m is expressed in moles per 1,000 g. of water, but in dilute solution this concentration unit will not differ materially from the concentration unit (moles per liter of solution) used by MacInnes and Shedlovsky. The thermodynamic equation for the e.m.f. of cell (A) is

$$E = E^\circ - \frac{RT}{F} \ln \gamma_{\mathrm{H^+}}\gamma_{\mathrm{Cl^-}}m_{\mathrm{H^+}}m_{\mathrm{Cl^-}}, \qquad (11)$$

[compare Eq. (18), Chap. XVI]

* H. S. Harned and B. B. Owen, *J. Am. Chem. Soc.*, **52**, 5079 (1930).

† H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **54**, 1350 (1932); see similar experiments on chloracetic acid by D. D. Wright, *ibid.*, **56**, 314 (1934).

where E° is the standard electrode potential of the cell

$$\text{Pt, } H_2 \mid HCl(m) \mid AgCl \mid Ag. \tag{B}$$

The thermodynamic equation for the dissociation of acetic acid is

$$K = \frac{\gamma_{H^+}\gamma_{OAc^-}m_{H^+}m_{OAc^-}}{\gamma_{HOAc} \cdot m_{HOAc}}. \tag{12}$$

In Eqs. (11) and (12) γ and m are substituted for **f** and c because of the different concentration unit. Harned and Ehlers eliminated m_{H^+} from Eqs. (11) and (12), obtaining

$$E - E^\circ + \frac{RT}{F}\ln\frac{m_{HOAc}m_{Cl^-}}{m_{OAc^-}} = \frac{-RT}{F}\ln\frac{\gamma_{H^+} \cdot \gamma_{Cl^-}\gamma_{HOAc}}{\gamma_{H^+} \cdot \gamma_{OAc^-}} - \frac{RT}{F}\ln K. \tag{13}$$

The quantities $\gamma_{H^+} \cdot \gamma_{Cl^-}/\gamma_{H^+} \cdot \gamma_{OAc^-}$, and γ_{HOAc} are nearly unity and equal unity at zero concentration. The logarithm of these quantities will vary slightly and nearly linearly with the ionic strength. (See Chap. XVII for a definition of the ionic strength.) Hence if

$$E - E^\circ + \frac{RT}{F}\ln\frac{m_{HOAc}m_{Cl^-}}{m_{OAc}} \tag{14}$$

be plotted against the ionic strength μ, the intercept at μ equals zero will be $-(RT/F)\ln K$, from which K may easily be computed. If Eq. (14) is set equal to $-(RT/F)\ln K'$ and K' plotted against the ionic strength, the intercept at μ equals zero will be equal to K directly. This second method of determining K is the method used by Harned and Ehlers. To evaluate Eq. (14) it is necessary to know E° at the different temperatures. Harned and Ehlers determined E° from measurements of cell (B) in the manner described in Chap. XVI. The quantity m_{Cl^-} is known from the composition of the solution, while m_{HOAc} equals $m_1 - m_{H^+}$ and m_{OAc^-} equals $m_2 + m_{H^+}$. The values of m_1 and m_2 are the stoichiometrical concentrations of acetic acid and sodium acetate, respectively. In order to find m_{H^+} Harned and Ehlers assumed an approximate value of K and then calculated m_{H^+} from Eq. (12). Knowing m_{H^+}, m_{OAc} and m_{HOAc} are readily computed and Eq. (14) in this way evaluated. Harned and Ehlers point out that the value of Eq. (14) is not very sensitive to the actual value of K used to compute m_{H^+}, so that

an approximate calculation of m_{H^+} is sufficient. After Eq. (14) had been evaluated, Harned and Ehlers calculated K', since $-(RT/F) \ln K'$ equals Eq. (14). On plotting K' against μ, a slightly curved line was obtained which on extrapolation to zero ionic strength gave the value of the true dissociation constant K. Their results are summarized in Table III.

TABLE III.—THE DISSOCIATION CONSTANT OF ACETIC ACID AT VARIOUS TEMPERATURES

Temp.	0°	5°	10°	15°	20°	25°	30°	35°
$K \times 10^5$	1.653	1.699	1.727	1.743	1.751	1.754	1.755	1.750

Harned and Ehlers's value at 25°C., 1.754×10^{-5}, agrees almost exactly with the value found by MacInnes and Shedlovsky by the conductance method, 1.753×10^{-5}.

At this point it is interesting to point out that the increase in heat content of the system, ΔH, for the dissociation may be calculated for acetic acid from the data in Table III by means of the van't Hoff equation of the reaction isochore. Equation (20), Chap. XVI, is

$$nFE^\circ = RT \ln K. \qquad \text{(XVI-20)}$$

Differentiating this equation with respect to temperature, we obtain

$$nF\frac{dE^\circ}{dT} = R \ln K\frac{dT}{dT} + RT\frac{d\ln K}{dT}. \qquad (15)$$

The Gibbs-Helmholtz equation is

$$nFE^\circ + \Delta H = nFT\frac{dE^\circ}{dT}. \qquad \text{(XVI-4)}$$

Eliminating $nF\frac{dE^\circ}{dT}$ and nFE° from equation (XVI-4) by means of Eqs. (15) and (XVI-20), the van't Hoff reaction isochore equation results,

$$RT \ln K + \Delta H = RT \ln K + RT^2\frac{d \ln K}{dT}$$

or

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}. \qquad (16)$$

Equation (16) tells us that if the dissociation constant becomes greater with rise of temperature, the heat content of the system will increase; that is, the reaction of dissociation will absorb heat. If the dissociation decreases with rise of temperature, heat will be liberated. These relationships could have been predicted also by the principle of Le Chatelier, but if $d \ln K/dT$ is known accurately, the heat of dissociation may be calculated. In the case of acetic acid the dissociation will be endothermic from 0° to 25°C., between 25° and 30°C. the heat of dissociation will be nearly zero, while between 30° and 35°C. the reaction will be exothermic.

The Dissociation Constant of Dibasic Acids.—Dibasic acids may be divided roughly into two classes, those whose "first" hydrogen is completely dissociated, and those whose first hydrogen is not completely dissociated. Sulfuric acid is an example of the first class, and sulfurous acid is an example of the second class. Sherrill and Noyes* have made a study of these acids, employing the modern method for the determination of the dissociation constants. Let us consider sulfuric acid first. The dissociation of sulfuric acid is given by the equations

$$H_2SO_4 \rightarrow H^+ + HSO_4^-$$
$$HSO_4^- \rightleftarrows H^+ + SO_4^=.$$

The first reaction is assumed to be complete, an assumption which the results of Sherrill and Noyes seem to justify. To calculate α, the degree of dissociation of the acid HSO_4^-, Sherrill and Noyes made use of the following equations for the molal conductance $\bar{\Lambda}$ of the acid and for the transference number of the hydrogen ion, t_{H^+}:

$$\bar{\Lambda} = (1 + \alpha)\bar{\Lambda}_{H^+} + (1 - \alpha)\bar{\Lambda}_{HSO_4^-} + \alpha\bar{\Lambda}_{SO_4^=}, \tag{17}$$

$$t_{H^+} = \frac{(1 + \alpha)\bar{\Lambda}_{H^+} - (1 - \alpha)\bar{\Lambda}_{HSO_4^-}}{\bar{\Lambda}}. \tag{18}$$

In Eqs. (17) and (18) $\bar{\Lambda}$ represents the molal conductance. Equations (17) and (18) were solved for α, the result being

$$\alpha = \frac{\Lambda + \Lambda t_{H^+} - \Lambda_{H^+}}{\Lambda_{H^+} + \Lambda_{SO_4^=}}. \tag{19}$$

* M. S. Sherrill and A. A. Noyes, *J. Am. Chem. Soc.*, **48**, 1861 (1926).

According to the conventions used in Chap. IV Λ and Λ_i represent the equivalent acid and ionic conductances, respectively. Interpolated values of Λ_{H^+} and $\Lambda_{SO_4^=}$ at the proper ionic concentration were used to calculate values of α(t_{H^+} for sulfuric acid is independent of the concentration, having the value 0.816); knowing α, the dissociation constant K_c could be calculated. Sherrill and Noyes also introduced the activity coefficients in the mass action expression

$$K = \frac{c_{H^+} \cdot c_{SO_4^=} \cdot f_{H^+} \cdot f_{SO_4^=}}{c_{HSO_4^-} \cdot f_{HSO_4^-}}$$

in order to calculate the true degree of dissociation. Their results are given in Table IV.

TABLE IV.—DEGREE OF DISSOCIATION AND DISSOCIATION CONSTANTS FOR HSO_4^- AT 25°C.

c	α	K_c	K
0.00025	0.959	0.0118	0.0105
0.001	0.874	0.0130	0.0105
0.005	0.668	0.0168	0.0112
0.00625	0.632	0.0175	0.0113
0.0125	0.522	0.0208	0.0119
0.025	0.423	0.0260	0.0130

It is interesting to note that K remains nearly constant while K_c varies by over 100 per cent. Sherrill and Noyes conclude that 0.0115 is the best value for the true dissociation constant of HSO_4^-.

In the above case of sulfuric acid the dissociation of the first hydrogen being practically complete, the conductance data were used to calculate the dissociation constant for the dissociation of the second hydrogen. In the case of sulfurous acid, however, the dissociation of the first hydrogen is small so that sulfurous acid may be considered a weak acid. The dissociation of the second hydrogen at moderate concentrations is so small that it may be neglected altogether. The dissociation of sulfurous acid may be represented, therefore, by the equation

$$H_2SO_3 \rightleftarrows H^+ + HSO_3^-,$$

and the dissociation constant for this reaction may be determined in the same way that it is determined for acetic acid.

In case the dissociation constant of the second stage of the dissociation is desired, conductance measurements are usually carried out on the sodium acid salt, $NaHA$, where A represents any anion.* The salt dissociates according to the equations

$$NaHA \rightarrow Na^+ + HA^-$$
$$HA^- \rightleftarrows H^+ + A^-.$$

The molal conductance is given by the equation

$$\bar{\Lambda} = \Lambda_{Na^+} + (1 - \alpha)\Lambda_{HA^-} + \alpha\Lambda_{H^+} + \alpha\bar{\Lambda}_{A^-}.$$

If the molal ionic conductances are known, α may be calculated and from α, the dissociation constant. The above equation neglects the formation of any H_2A. McCoy† has described a rather complicated procedure for calculating the hydrogen ion concentration in solutions of an acid salt. When values of c_{H^+} in acid salt solutions are known, the second dissociation constant, K_2, may be calculated since Noyes‡ has shown that the second dissociation constant can be calculated from the equation

$$K_2 = \frac{(K_1 + c + c_{H^+})c_{H^+}^2}{K_1(c - c_{H^+})} \tag{20}$$

if the first dissociation constant of the acid, K_1, is known. In Eq. (20), c is the concentration of the acid salt, and c_{H^+} is the concentration of the hydrogen ion in solutions of the acid salt.

The dissociation constants of dibasic acids may also be calculated from e.m.f. measurements of the appropriate cells. As a good example of such calculations the recent extensive work of MacInnes and Belcher§ on the dissociation constants of carbonic acid can be quoted. They studied cells of the type

Ag | AgCl | 0.01 N HOAc, 0.01 N KOAc, 0.01 N KCl | glass (*C*)
(hydrogen) electrode | $KHCO_3$, KCl, CO_2 (dissolved) | AgCl | Ag

* CHANDLER, *J. Am. Chem. Soc.*, **30**, 694 (1908).

† H. N. McCOY, *J. Am. Chem. Soc.*, **30**, 692 (1908).

‡ A. A. NOYES, *Z. physik. Chem.*, **11**, 495 (1893).

§ D. A. MACINNES and DONALD BELCHER, *J. Am. Chem. Soc.*, **55**, 2630 (1933); see Nims, *ibid.*, **56**, 1110 (1934), for experiments measuring K_1 for H_3PO_4.

in which the concentrations of $KHCO_3$ and KCl were equal and in which the carbon dioxide in the solution was in equilibrium with the gas at a known partial pressure. The glass electrode may be treated as a hydrogen electrode; it has the great practical advantage in this case that no hydrogen gas is necessary (see Chap. XXV for a detailed discussion of the glass electrode). Since the solubility of carbon dioxide follows Henry's law, it is possible to calculate values of K_c for the L.M.A.

$$K_1 = \frac{c_{H^+} \cdot c_{HCO_3^-}}{c_{CO_2}} \cdot \frac{f_{H^+} \cdot f_{HCO_3^-}}{f_{CO_2}},$$

which when extrapolated to infinite dilution yield true values of K_1. The second dissociation constant given by the equation,

$$K_2 = \frac{c_{H^+} \cdot c_{CO_3^=}}{c_{HCO_3^-}} \cdot \frac{f_{H^+} \cdot f_{CO_3^=}}{f_{HCO_3^-}}$$

was obtained from calculations involving the e.m.f. of cells similar to cell (C) except that the dissolved carbon dioxide was replaced by potassium carbonate.* At 25°C. they find K_1 and K_2 to be 4.54×10^{-7} and 5.61×10^{-11}, respectively.

Summary of Dissociation Constants.—Table V includes dissociation constants calculated by modern methods, *i.e.*, by the method of Davies, MacInnes, and of Sherrill and Noyes, or by methods that involve e.m.f. measurements such as the method described above of Harned and Owen, or by potentiometric methods that estimate the dissociation constants from the shape of titration curves. The electrometric titration curve method will be described in Chap. XXIV.† Randall and Allen‡ also describe a method for the determination of the dissociation constant of weak electrolytes from freezing-point data. Gane and

* The calculations as carried out by MacInnes and Belcher were not quite so simple as might be inferred from the above discussion. They had to make several corrections to their equations such as the correction due to the hydrolysis of potassium carbonate. It is left as a problem to the student to derive the necessary functions which on extrapolation will yield the desired values of K_1 and K_2.

† See F. L. Hahn and R. Klockmann, *Z. physik. Chem.*, **146A**, 373 (1930).

‡ M. Randall and C. Allen, *J. Am. Chem. Soc.*, **52**, 1814 (1930).

TABLE V.—DISSOCIATION CONSTANTS OF WEAK ELECTROLYTES*

Substance	Temp.	$K_1 \times 10^5$	$K_2 \times 10^{11}$	Reference
Inorganic acids				
HSO_3^-	25	1150.0		S and N
H_2SO_3	25	1200.0		S and N
H_3PO_4	18	830.0		S and N
HIO_3	25	17300.0		D
H_2CO_3	25	0.0454	5.61	Mac I. and B.
Inorganic and organic bases†				
NH_3	25	1.79		H and O
CH_3NH_2	25	43.8		H and O
$(CH_3)_2NH$	25	52.0		H and O
$(CH_3)_3N$	25	5.45		H and O
$(CH_3)_4NOH$	Strong base like KOH			
Organic acids				
Formic	25	17.7		H and O
Acetic	25	1.75		MacI.
Cyanacetic	25	350		MacI.
Benzoic	25	6.312		B. and K.
Cyanbenzoic	25	31.0		K. W. and L.
o-Chlorobenzoic	25	122		MacI.
o-Nitrobenzoic	25	600		MacI.
3, 5 Dinitrobenzoic	25	150		MacI.

* References for Table V are as follows: S. and N., SHERRILL and NOYES, *loc. cit.;* D., DAVIES, *loc. cit.;* MACI., D. A. MACINNES, *loc. cit.;* H. and O., HARNED and OWEN, *loc. cit.;* K. W. and L., H. D. KIRSCHMAN, B. WINGFIELD and H. J. LUCAS, *J. Am. Chem. Soc.* **52**, 23 (1930); MACI. and B., MACINNES and BELCHER, *loc. cit.;* B. and K., BROCKMAN and KILPATRICK, *loc. cit.*

† See N. F. HALL and M. R. SPRINKLE, *J. Am. Chem. Soc.*, **54**, 3469 (1932), for a comprehensive study of the strength of organic bases in aqueous solution.

Ingold* have estimated the true dissociation constants for the dissociation of the first and second hydrogens of a number of organic acids by calculating the dissociation constant at various concentrations from potentiometric titration curves and extrapolating the values to zero concentration. Their data are collected in Table VI.

* R. GANE and C. K. INGOLD, *J. Chem. Soc.*, **1931**, 2153. See also V. SIHVONEN, *Z. Elektrochem.*, **36**, 165 (1930).

TABLE VI.—DISSOCIATION CONSTANTS OF DIBASIC ACIDS AT 25°C.

Acid	$K_1 \times 10^4$	$K_2 \times 10^7$
Oxalic	590	640
Malonic	14.9	20.3
Substituted malonic acids		
methyl-	8.92	17.5
ethyl-	10.3	14.7
n-propyl-	10.1	14.3
iso-propyl-	11.4	13.2
dimethyl-	6.83	8.72
methylethyl	13.8	3.86
diethyl	61.5	0.51
ethyl-*n*-propyl-	71.6	0.37
di-*n*-propyl	85.8	0.31
Succinic	0.641	33.3
Substituted succinic acids		
$\alpha\alpha'$-dimethyl (209)	1.70	11.6
$\alpha\alpha'$-dimethyl (129)	1.15	6.36
$\alpha\alpha'$-diethyl (192)	2.33	3.47
$\alpha\alpha'$-diethyl (129)	3.11	2.54
tetramethyl	3.19	0.52
Glutaric	0.453	38
Substituted glutaric acids		
β-methyl-	0.565	5.96
β-ethyl-	0.517	4.69
β-*n*-propyl-	0.487	4.11
$\beta\beta$-dimethyl-	1.98	5.10
$\beta\beta$-methylethyl	2.40	2.00
$\beta\beta$-diethyl	2.38	0.75
$\beta\beta$-di-*n*-propyl	2.05	0.49

For references to dissociation constants of other organic compounds (determined by classical methods) see Scudder,* or Vol. VI of the "International Critical Tables."

Practical Application of the Dissociation Constant.—A knowledge of the dissociation constants of acids and bases is useful in enabling a comparison of the strength of different acids or of different bases to be made. The dissociation constant is a good measure of the strength of an acid; it is directly related to the free energy of ionization, the smaller the dissociation constant, the greater is the free energy which must be added to the system

* H. SCUDDER, "The Electrical Conductivity and Ionization Constants of Organic Compounds," D. Van Nostrand Company, New York, 1914.

in order to convert the undissociated molecules in their standard state to ions in their standard states. If an acid is quite weak, the L.M.A. reduces to the simple expression

$$\alpha = \sqrt{\frac{K}{c}},$$

where α is the degree of dissociation. If we compare two weak acids at the same concentration c, the ratio of their degrees of dissociation is equal to the ratio of the square roots of their dissociation constants, or

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_1}{K_2}}.$$

Dissociation constants of acids and bases are useful in calculating the extent of hydrolysis of salts, in calculating the shape of titration curves, in helping us to prepare suitable buffer solutions and in theories and classifications of indicators. In the next chapter we shall consider more in detail these practical applications of the dissociation constant for aqueous solutions. Before considering dissociation constants in nonaqueous solutions and the general significance of acidity in these solvents, we shall describe the relations, if any, that exist between chemical constitution and dissociation constant in aqueous solutions.

Relation between Chemical Constitution and Dissociation Constant.—There are many interesting relations that exist between the chemical constitution of acids and their dissociation constants, although the theoretical significance of these relationships is yet far from clear. The chlorine substituted fatty or aliphatic acids have been discussed by Langmuir.* Langmuir points out that if one of the hydrogen atoms in the methyl group of acetic acid is replaced by a chlorine atom to form chloroacetic acid, the electrons in the carboxyl group tend to shift in the direction of the chlorine atom. This is because the chlorine atom has a greater tendency to take on electrons than the hydrogen atom which it displaces. The shift of electrons in the carboxyl group toward the chlorine atom makes it easier for the hydrogen nucleus which is bound to the carboxyl group to pass over to a water molecule to form the hydrogen ion in solution

* I. Langmuir, *Chem. Rev.*, **6**, 465 (1929).

(H_3O^+). Substitution of additional chlorine atoms increases the dissociation constant. The dissociation constants K_c of some chlorine-substituted fatty acids are given in Table VII (quoted from Langmuir's paper).

TABLE VII.—DISSOCIATION CONSTANTS OF CHLORINE-SUBSTITUTED FATTY ACIDS

Acid	$K_c \times 10^5$	ln r	Volts
Acetic	1.85	[0]	0
Chloroacetic	155.0	4.44	0.1053
Dichloroacetic	5000.0	7.6	0.190
Trichloroacetic	20000.0	9.3	0.233
Propionic	1.4	[−0.26]	−0.006
α-chloropropionic	147.0	4.36	0.1045
β-chloropropionic	8.6	1.53	0.0382
Butyric	1.5	[−0.21]	−0.0053
α-chlorobutyric	139.0	4.30	0.1038
β-chlorobutyric	8.9	1.57	0.0392
γ-chlorobutyric	3.0	0.48	0.012

From Table VII we learn that the nearer the chlorine atom is to the carboxyl group the greater is the dissociation constant, and the greater the number of substituted chlorine atoms, the greater is the dissociation constant. The values of K_c given in Table VII are not corrected for the variation of ionic mobilities and activity coefficients with concentration, but the general conclusions which Langmuir arrived at will not be invalidated for this reason.

It will be remembered that the natural logarithm of the dissociation constant is related to the free energy by the equation (for a single molecule)

$$-\Delta G^\circ = kT \ln K. \tag{21}$$

Langmuir subtracts the value of ln K_c for acetic acid from the values of ln K_c for all the other acids to obtain the values of ln r given in Table VII. Stated in other words, r is the ratio of K_c for the acid in question to K_c for acetic acid. The Boltzmann equation (see Chap. XVIII) relates the difference in work necessary to remove the hydrogen ion from the given acid molecules

and from an acetic acid molecule with the relative numbers of hydrogen ions in these two positions,

$$\frac{n_2}{n_1} = e^{\frac{\lambda}{kT}}. \tag{22}$$

Ln r must be equal to $2\lambda/kT$, since from Eq. (21) $kT \ln r$ is equal to $(\Delta G^{\circ\cdot\prime} - \Delta G^{\circ\cdot\prime\prime})$ and λ is the difference in work necessary to remove the hydrogen ion from the two different acid molecules. Langmuir obtains 2λ in volts by multiplying $\ln r$ by 0.025, the value of kT in volts. The right-hand column of Table VII contains 2λ in volts, and from this table several interesting relations can be observed. If the monochloro acids in which the chlorine group is in the α position are compared, it is found that 2λ is nearly the same for all, 0.105 v. The two β-monochloro acids give 2λ equal to 0.039 v., and the γ-chlorobutyric acid gives 2λ equal to 0.012 v. The difference in energies declines as the chlorine atom is substituted in a position farther away from the carboxyl group.

Langmuir also points out that we should expect the effect of substitution of the chlorine atom to decrease exponentially with distance along the carbon chain. Thus, substitution in the β position should decrease the value of 2λ as compared with 2λ for the α substituted acid in the ratio of 2.7:1. The data of Table VII bear out this conclusion roughly.

MacInnes* has discovered an interesting empirical relationship between the logarithm of the dissociation constant of the acid and the position in which the chlorine atom is substituted. He plots the logarithm of the dissociation constant against $1/d$ in which $d = 1$ for the α position, 2 for the β position, 3 for the γ position, and so forth. Such a plot for monochloro-substituted acids is illustrated in Fig. 2. Hydroxyl-substituted acids give data that agree with this relationship, but bromo- and iodo-substituted acids do not agree quite so well. MacInnes's interpretation of this relationship is as follows: The mutual potential energy of two equally charged spheres on bringing them near to each other is given by the equation

$$U = C'\frac{1}{d}, \tag{23}$$

* D. A. MacInnes, *J. Am. Chem. Soc.*, **50**, 2587 (1928); Harned and Embree have recently published an empirical law relating dissociation constants and temperature [*ibid.*, **56**, 1050 (1934)].

where U is the energy, C' is a constant, and $1/d$ is the distance between the charges. MacInnes infers by analogy that there is some relationship between Eq. (23) and his empirical equation,

$$\log K_c = C + S\frac{1}{d}. \tag{24}$$

The difficulty of this interpretation is that there is no reason for believing that Eq. (23) accurately reproduces the potential energy in molecules. Smallwood* has recently attempted to calculate theoretically the change in dissociation constant of organic acids as various polar groups are substituted into the acid. He makes use of the known electric moments (see Chap. XII) of the substituted groups and also considers their orientation in his theory. The calculated results indicate that other factors must be considered in addition to the electric moment of the substituted group.

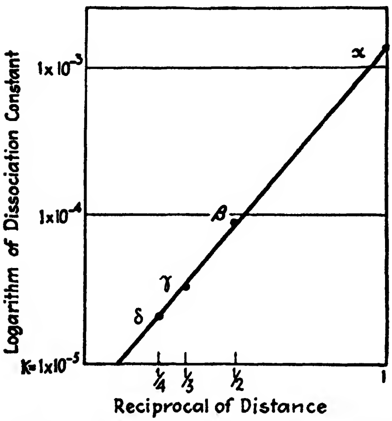

FIG. 2.—Test of the MacInnes relation for the chlorine-substituted acids.

It is interesting to compare the dissociation constants of the bases listed in Table V. In the case of all except the last, there are two equilibria involved when these bases are dissolved in water. Let us consider the most common base, ammonia. When ammonia dissolves in water, we have the following reactions taking place,

$$NH_3 + H_2O \rightleftarrows NH_4OH \tag{25}$$

and

$$NH_4OH \rightleftarrows NH_4^+ + OH^-. \tag{26}$$

The question which now arises is: Are we measuring the dissociation constant of reaction (25) or of (26) in our conductance measurements? There is good reason to believe that NH_4OH is a strong base as such and is dissociated to the extent that

* H. M. SMALLWOOD, *J. Am. Chem. Soc.*, **54**, 3048 (1932). See also BJERRUM, *Z. physik. Chem.*, **106**, 219 (1923); BRIEGLEB, *Z. physik. Chem.*, **10B**, 205, (1931).

sodium hydroxide is dissociated. We think that this is the case because tetramethyl ammonium hydroxide is a very strong base. It cannot undergo a reaction similar to (25) and therefore is a strong base.

Hall and Sprinkle* call attention to the fact that *dialkyl*-substituted bases are much stronger than either mono- or trialkyl-substituted bases. (Compare K_B for CH_3NH_2 and $(CH_3)_2NH$, Table V). Hall and Sprinkle also point out that the nitro-, chloro-, and bromo-substituted groups decrease the strength of bases, as do the second and third substituted ethanol and phenyl groups when substituted into ammonia. The methoxy and ethoxy groups increase the strength of aniline if substituted in the ortho or meta position. Saturation of the aromatic nucleus increases the strength of the base. As yet, however, there is no theoretical interpretation of these interesting observations.

Dissociation Constants in Nonaqueous Solutions.—We have already mentioned in Chaps. II and V the fact that it is possible to show a definite relationship between the dissociation constant of tetraisoamylammonium nitrate in dioxane-water mixtures and the dielectric constant of these mixtures, provided the dielectric constant is 38 or below. Above a value of 38 the salt is apparently completely dissociated; its dissociation constant approaches infinity at a value of the dielectric constant equal to 43.6.

The dissociation constants of other substances may be readily determined in nonaqueous solutions by making conductance measurements over a series of concentrations. As an example, we may quote the recent experiments of Shedlovsky and Uhlig† on solutions of sodium and potassium quaiacolates in quaiacol. Many interesting data have been collected in the field of nonaqueous solutions; we shall describe here, however, only the more important experiments which give us information concerning the strength of acids and bases in these solvents. Not only are we interested in the relative strength of acids and bases in a given solvent, but we are also interested in the relative acidity of the same acid in different solvents. We have already seen that the square root of the ratio of the dissociation constant of two weak

* N. F. Hall and M. R. Sprinkle, *J. Am. Chem. Soc.*, **54**, 3469 (1932).
† T. Shedlovsky and H. H. Uhlig, *J. Gen. Physiol.*, **17**, 549 (1934).

acids in water is a measure of the relative acid strength of the two solutions, but this is not necessarily true if the two solutions which we compare are formed from two different solvents. In the case of nonaqueous solutions we need to introduce new concepts and new definitions in order to understand the meaning of acidity in these solutions. The most general and the most commonly accepted definition of acids and bases is that of Brønsted which will now be described.

The Brønsted Concept of Acids and Bases.—An acid in aqueous solutions is usually considered to be a substance which gives hydrogen ions on dissociation. A base in aqueous solutions is usually considered to be a substance which gives hydroxyl ions on dissociation while neutralization is usually considered to be the reaction between an acid and a base to give a salt plus water, or more simply the combination of a hydrogen ion with a hydroxyl ion to form water. But there are many solvents in which acids may be neutralized by bases which contain no hydroxyl ion. Conversely it is possible to demonstrate the existence of acid reactions due to substances other than the hydrogen ion. Before giving examples of these interesting substances, let us consider just what we mean by the hydrogen ion. Hitherto in this book we have used the term hydrogen ion without giving it any definite meaning; in fact, it has been unnecessary to do so inasmuch as we have always spoken of the hydrogen ion in its stoichiometric sense. That is, in speaking of the concentration of the hydrogen ion, for example, we mean the concentration of the hydrogen ion which we determine analytically, etc. Now, however, we must become explicit.

When dry hydrogen chloride gas is passed into water, the following reaction undoubtedly occurs:

$$HCl + H_2O \rightleftarrows H_3O^+ + Cl^-. \qquad (27)$$

Hydrogen chloride does not dissociate into the chloride ion and the unhydrated proton, because the proton cannot exist free in solution; it attaches itself to a water molecule and may be considered as being rather deeply buried in a water molecule since its size is so small in relation to its charge. There are many lines of evidence which lead to the belief that the proton cannot exist in the unhydrated condition (in this connection see the discussion of the glass electrode, Chap. XXV). Probably there

are no solutions in which free protons can exist in appreciable concentration; the proton may have a transitory existence, however, since we believe that the hydrogen ion is largely transported through aqueous solutions by virtue of spontaneous transfers of protons between water molecules. The hydrogen ion H_3O^+ may be further hydrated in the same way that other ions such as the potassium ion are hydrated.

What happens on neutralization? The addition of a base will cause the following reaction to occur:

$$H_3O^+ + OH^- \rightarrow 2H_2O. \tag{28}$$

The protons in the hydrogen ion are in a much higher level of energy than is the single proton in the hydroxyl ion and, as a consequence, the extra proton of the hydrogen ion will make an irreversible transfer to the hydroxyl ion with the liberation of a considerable amount of energy. It is possible to reduce the hydrogen ion concentration in different ways by the addition of substances other than the hydroxyl ion. If acetate ions, for example, are added to the solution, the hydrogen ion concentration will fall due to the reaction

$$H_3O^+ + CH_3OOO^- \rightarrow CH_3COOH + H_2O, \tag{29}$$

where the extra proton of the H_3O^+ ion now finds a position of lower energy in the acetate ion. Are we to consider the acetate ion as being a base similar to the hydroxyl ion? In anhydrous acetic acid solutions Hall and Conant* have carried out titrations of dry hydrogen chloride with dry sodium acetate obtaining results entirely comparable with those obtained in titrating hydrochloric acid with sodium hydroxide in water. No water is formed in this neutralization reaction, yet the reaction is apparently a true neutralization reaction.

Similarly it is possible to diminish the concentration of the hydroxyl ion without the addition of the hydrogen ion in a reaction such as

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O. \tag{30}$$

In this reaction the hydroxyl ion is neutralized partially without the addition of the hydrogen ion. Shall we call the ammonium ion an acid? It must be obvious by now that the old formula-

* N. F. Hall and J. B. Conant, *J. Am. Chem. Soc.*, **49**, 3047 (1927).

tion of acids and bases by means of the hydrogen and hydroxyl ions is inadequate since we can have many reactions in which the acidity or basicity is altered by the addition of substances other than these ions.

Brønsted* proposed that acids and bases be defined by means of the equation

$$A \rightleftarrows B + p^+ \tag{31}$$

where p^+ is the proton, A the acid, and B the base. A and B may have any charges as long as A is one unit more positive than B. An acid is to be considered, therefore, as a proton donor and a base as a proton acceptor. This definition is remarkably simple, yet it is perfectly general and has been of immense help in aiding us to understand acid-base reactions not only in non-aqueous solutions but also in water. Let us now consider some actual reactions. [The reaction represented by Eq. (31) cannot be carried out independently of some other reaction due to the fact that protons cannot exist uncombined.] In the reaction

$$HCl + H_2O \rightleftarrows H_3O^+ + Cl^- \tag{27}$$

water is the base because it has taken on a proton while hydrogen chloride is the acid because it has given up a proton. In reaction (29) the hydrogen ion is the acid and the acetate ion is the base because the proton passes from the hydrogen ion to the acetate ion. Water may be both a base or an acid depending upon the reaction. In reaction (27) it is a base while in the reaction

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \tag{32}$$

it is an acid (proton donor). At this point it is interesting to point out that all the strong acids have about the same acidity in water because they are all practically completely decomposed forming in each case the acid H_3O^+; thus

$$\begin{aligned} &HCl && + H_2O \rightarrow H_3O^+ + Cl^- \\ &HBr && + H_2O \rightarrow H_3O^+ + Br^- \\ &HI && + H_2O \rightarrow H_3O^+ + I^- \end{aligned}$$

* J. N. Brønsted, *Rec. Trav. Chim. Pays-Bas*, **42**, 43, 1048 (1923); *Chem. Rev.*, **5**, 284 (1928); *J. Phys. Chem.*, **30**, 777 (1926); see also Lowry, *Chem. & Ind.*, **42**, 43 (1923); N. F. Hall has briefly reviewed the subject in *J. Chem. Ed.*, **7**, 782 (1930). For a recent discussion see Brønsted, *Z. physik. Chem.*, **169A**, 52 (1934).

$$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$$
$$HClO_4 + H_2O \rightarrow H_3O^+ + ClO_4^-.$$

In concentrated aqueous solutions and in nonaqueous solutions where the above reactions do not go so nearly to completion, individual differences between the strong acids are much more pronounced.

It is possible to have acids other than the hydrogen ion in aqueous solution; Kilpatrick and Rushton* have demonstrated the existence of the reaction

$$\tfrac{1}{2}Mg + HCOOH \rightarrow \tfrac{1}{2}Mg^{++} + \tfrac{1}{2}H_2 + HCOO^- \qquad (33)$$

as well as the usual reaction

$$\tfrac{1}{2}Mg + H_3O^+ \rightarrow \tfrac{1}{2}Mg^{++} + H_2O + \tfrac{1}{2}H_2. \qquad (34)$$

In Eq. (33) the HCOOH molecule is the acid since it loses a proton during the reaction.

In nonaqueous solutions we can write such reactions as

1. acetic acid as solvent

$$\underset{\text{(acid)}}{HCl} + \underset{\text{(base)}}{CH_3COONa} \rightarrow NaCl + CH_3COOH,$$

2. liquid ammonia as solvent

$$\underset{\text{(acid)}}{CH_3CONH_2} + \underset{\text{(base)}}{KNH_2} \rightarrow CH_3CONHK + NH_3,$$

3. hydrogen fluoride as solvent

$$\underset{\text{(acid)}}{HF} + \underset{\text{(base)}}{HNO_3} \rightarrow H_2NO_3^+ + F^-.$$

In the hydrogen fluoride reaction the strong acid HNO_3 acts as a base since hydrogen fluoride is a stronger proton donor than is nitric acid. Perhaps these reactions are sufficient in number to show the general applicability of the proton donor and acceptor theory of acids and bases. Let us now formulate mathematically the equilibria which have been described above.

* M. Kilpatrick, Jr. and J. H. Rushton, *J. Phys. Chem.*, **34**, 2180 (1930); **38**, 269 (1934).

Following Brønsted* let us take as the measure of the strength of acids and bases the "acidity" and "basicity" so-called exhibited by the solutions when the ratio between the concentrations of acid and base is unity. Referring to Brønsted's scheme of definition of acids and bases, Eq. (31),

$$A \rightleftarrows B + p^+,$$

we can write the expression

$$\frac{c_B}{c_A} \cdot c_{p^+} \, . \, \mathrm{f}_{p^+} = K_{acid.}, \tag{35}$$

where c_B and c_A are the stoichiometric concentrations of the base and acid. When the ratio c_B/c_A is unity, $K_{acid.}$ equals the acidity, $c_{p^+} \cdot \mathrm{f}_{p^+}$. For bases Brønsted writes the equation

$$\frac{c_A}{c_B} \frac{1}{c_{p^+} \cdot \mathrm{f}_{p^+}} = K_{bas.}. \tag{36}$$

The constants defined by Eqs. (35) and (36) are called the acidity constant and basicity constant, respectively. These equations merely define $K_{acid.}$ and $K_{bas.}$; they are not thermodynamic L.M.A. equations. Brønsted also defined acidity and basicity constants for the medium as illustrated in the following example: The acid function for water is

$$H_2O \rightarrow OH^- + p^+ \tag{37}$$

for which Brønsted defines the acidity constant $K_{acid.(H_2O)}$, given by the equation

$$c_{OH^-} \cdot c_{p^+} \cdot \mathrm{f}_{p^+} = K_{acid.(H_2O)}. \tag{38}$$

The base function for water is

$$H_2O + p^+ \rightarrow H_3O^+, \tag{39}$$

for which Brønsted defines the basicity constant $K_{bas.(H_2O)}$, by the equation

$$c_{H_3O^+} \cdot \frac{1}{c_{p^+} \cdot \mathrm{f}_{p^+}} = K_{bas.(H_2O)}. \tag{40}$$

Brønsted calls the constants of Eqs. (38) and (40) the conventional acidity and basicity constants because the concentration of the water is omitted in the equations.

* J. N. Brønsted, *Chem. Rev.*, **5**, 291 (1928).

The acid and base acidity and basicity constants and the medium acidity and basicity constants are related to the usual acid and base dissociation constants by the equations

$$K_A = K_{acid.} \cdot K_{bas.\ (medium)} \tag{41a}$$
$$K_B = K_{bas.} \cdot K_{acid.\ (medium)}, \tag{41b}$$

where K_A and K_B are the usual acid and base dissociation constants. As an example of the use of these equations let us consider the two acids acetic acid and the ammonium ion in two solvents, water and methyl alcohol. For acetic acid, the usual dissociation may be described by the equation

$$HOAc + H_2O \rightleftarrows H_3O^+ + OAc^-, \tag{42}$$

for which we have the conventional L.M.A. constant K_A on leaving out the concentration of the solvent and the activity coefficients,

$$K_A = \frac{c_{H_3O^+} \cdot c_{OAc^-}}{c_{HOAc}}. \tag{43}$$

The acid function and corresponding equation defining K_{acid} for acetic acid are

$$HOAc \rightarrow p^+ + OAc^-, \tag{44}$$
$$K_{acid.} = \frac{c_{OAc^-} \cdot c_{p^+} \cdot \mathbf{f}_{p^+}}{c_{HOAc}}. \tag{45}$$

By multiplying Eq. (45) by Eq. (40) we obtain Eq. (43) in agreement with Eq. (41*a*).

For methyl alcohol solutions of acetic acid the following equilibria and equations can be written:

1. Acid function of methyl alcohol

$$CH_3OH \rightleftarrows p^+ + CH_3O^- \tag{46a}$$
$$K_{acid.(CH_3OH)} = c_{CH_3O^-} \cdot c_{p^+} \cdot \mathbf{f}_{p^+} \tag{46b}$$

2. Base function of methyl alcohol

$$CH_3OH + p^+ \rightarrow CH_3OH_2^+ \tag{47a}$$

$$K_{bas.(CH_3OH)} = c_{CH_3OH_2^+} \cdot \frac{1}{c_{p^+} \cdot \mathbf{f}_{p^+}} \tag{47b}$$

3. Dissociation of acetic acid

$$CH_3COOH + CH_3OH \rightarrow CH_3OH_2^+ + CH_3COO^- \tag{48a}$$

$$K_A = \frac{c_{CH_3OH_2^+} \cdot c_{CH_3COO^-}}{c_{CH_3COOH}} \tag{48b}$$

4. Acid function for acetic acid.

The acid reaction and equation defining $K_{acid.}$ are given by Eqs. (44) and (45).

In considering solutions of the ammonium ion in the solvents water and methyl alcohol we have to introduce the following additional equations and reactions.

1. Acid function of the ammonium ion.

$$NH_4^+ \rightarrow NH_3 + p^+ \tag{49a}$$

$$K_{acid.} = \frac{c_{NH_3} \cdot c_{p^+} \cdot \mathbf{f}_{p^+}}{c_{NH_4^+}}. \tag{49b}$$

2. Dissociation (or hydrolysis) of the ammonium ion in water.

$$NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+ \tag{50a}$$

$$K_A = \frac{c_{NH_3} \cdot c_{H_3O^+}}{c_{NH_4^+}}. \tag{50b}$$

By combining Eqs. (49*b*) and (40), Eq. (50*b*) is obtained in agreement with the relation expressed by Eq. (41*a*).

3. Dissociation (or alcoholysis) of the ammonium ion in methyl alcohol.

$$NH_4^+ + CH_3OH \rightarrow CH_3OH_2^+ + NH_3 \tag{51a}$$

$$K_A = \frac{c_{CH_3OH_2^+} \cdot c_{NH_3}}{c_{NH_4}}. \tag{51b}$$

By combining Eqs. (49*b*) and (47*b*), Eq. (51*b*) is obtained in agreement with Eq. (41*a*).

An interesting consequence of these relations of Brønsted follows from Eqs. (41*a*) and (41*b*). It is evident that $K_A/K_{acid.}$ must be the same for all acids in a given solvent and the ratio must change to the same extent for all acids if the solvent is changed.

As an example of the application of these equations Brønsted* quotes data obtained by Bjerrum, Unmack, and Zechmeister†

* J. N. Brønsted, *Chem. Rev.*, **5**, 310 (1928).

† Bjerrum, Unmack, and Zechmeister, *K. D. Vid. Selsk. Medd.*, **5**, No. 11 (1924).

on the dissociation of acetic acid and ammonia in methyl alcohol and of methyl alcohol itself and by Mitzutani* on the change in acidity constant of a series of acids from water to 95 per cent methyl alcohol. Bjerrum, Unmack, and Zechmeister obtained their dissociation constant by e.m.f. measurements of acid-base cells employing methyl alcohol as a solvent. They checked their results by measuring the alcoholysis of CH_3COONH_4 in methyl alcohol (for the relation of solvolysis to dissociation constant of solvent and acid or base concerned see the next chapter). Mitzutani obtained his results by making direct e.m.f. measurements of the acidity of equimolecular mixtures of the acid and the acid salt in the solvent. Such data are usually put in terms of pH units; these units are described in the next chapter and the method of measuring the pH in Chap. XXIV. Brønsted's calculations are given in Table VIII.

TABLE VIII

	K_A in CH_3OH	K_A in H_2O	$\Delta \log K_A$	$\Delta \log K_{acid.}$	$\Delta \log K_{bas.(med.)}$
Acetic acid......	$10^{-9.65}$	$10^{-4.76}$	-4.9	-2.3	-2.6
Ammonium ion..	$10^{-11.09}$	$10^{-9.39}$	-1.7	$+0.8$	-2.5
Difference between acetic acid and NH_4^+			-3.2	-3.1	

From Table VIII it is seen that the results of the two independent investigations agree with each other and that pure methyl alcohol is about 350 times as weak a base as is pure water. It should be pointed out, however, that the figures for $K_{acid.}$ are somewhat uncertain due to existence of a liquid-junction potential in the cell used to measure the acidity (pH).

Hall and Conant have carried out interesting electrometric titrations of acids and base in acetic acid as solvent. As will be shown in Chap. XXIV it is possible to calculate dissociation constants from these titration curves. They find from acidity measurements using a platinum-chloranil† electrode that per-

* M. MITZUTANI, *Z. physik. Chem.* **118**, 327 (1925).

† Chloranil is completely chlorinated quinone. The quinone and its hydroquinone constitute the electrode. See Chap. XXIV for a discussion of the analogous quinhydrone electrode.

chloric, sulfuric, and trichloroacetic acids (they call these solutions "superacid solutions") are much stronger in acetic acid than in water; and that whereas these acids are all of nearly equal strength in water their strengths in acetic acid differ materially. The superacidity of acetic acid solutions is explained by Conant and Hall* on the supposition (following Brønsted) that the ion $CH_3COOH_2^+$ more readily gives up its extra proton than does the ion H_3O^+.

Exercises

1. Shedlovsky and Uhlig give the following values for the equivalent conductances of sodium guaiacolate in wet guaiacol at 25°C. (dielectric constant of wet guaiacol is 14.3). Calculate the dissociation constant of sodium guaiacol in these solutions. The formula of this salt may be taken as NaG.

TABLE IX.—EQUIVALENT CONDUCTANCE OF SODIUM GUAIACOLATE IN WET GUAIACOL AT 25°C.

c	Λ
0	7.50
0.000206	2.893
0.000771	1.707
0.00224	1.097
0.00454	0.809
0.00901	0.601
0.01666	0.460

2. Calculate ΔH for the dissociation of acetic acid at 5°C. and at 30°C.
3. Derive Eq. (19).
4. Show mathematically the difference between Langmuir's and MacInnes's relations connecting the dissociation constant of the chlorine substituted acids with the position of the chlorine atom in the molecule.
5. Derive equations which will enable a calculation of K_1 and K_2 for carbonic acid to be made according to methods of Harned from the e.m.f. of the cells measured by MacInnes and Belcher. Assume that the constant of Henry's equation, $c_{CO_2} = kp_{CO_2}$, is known.

* N. F. HALL and J. B. CONANT, *J. Am. Chem. Soc.*, **49**, 3047 (1927); CONANT and HALL, *ibid.*, **49**, 3062 (1927); HALL and WERNER, *ibid.*, **50**, 2367 (1928).

CHAPTER XXI

HOMOGENEOUS IONIC EQUILIBRIA

II. AQUEOUS-SOLUTION EQUILIBRIA

The Dissociation Constant of Water.—Water is such an important solvent and the equilibria which exist in aqueous solution are so important from the chemical, industrial and physiological standpoints that it seems worthwhile to devote a chapter to the discussion of the various phenomena that may be observed in aqueous solution and to the elucidation of the mathematical relationships involved.

The dissociation constant of water can be measured accurately by at least two methods, and since this constant is an important quantity for all work in aqueous solutions, we shall consider the different methods for determining it.

The thermodynamic equation defining the dissociation constant of water is

$$K = \frac{N_{OH^-} \cdot N_{H^+} \cdot f_{OH^-} \cdot f_{H^+}}{N_{H_2O} \cdot f_{H_2O}} \tag{1}$$

where N is the mole fraction and f is the activity coefficient defined in terms of the mole fraction. Since N_{H_2O} and f_{H_2O} are nearly unity and do not vary appreciably with change of concentration (at least in dilute solutions), it is customary to write Eq. (2) instead of (1)

$$K = N_{OH^-} \cdot N_{H^+} \cdot f_{OH^-} \cdot f_{H^+}. \tag{2}$$

The mole fraction, however, is not extensively used as a concentration unit; let us use instead moles per liter of solution, we can then define the dissociation constant of water by the equation

$$K_w = c_{OH^-} \cdot c_{H^+} \cdot \mathrm{f}_{OH^-} \cdot \mathrm{f}_{H^+} \tag{3}$$

where c is the concentration in moles per liter and f is the activity coefficient defined in terms of moles per liter of solution. K_w is sometimes called the ionic product of water.

The dissociation constant for water may be calculated from conductance measurements or from e.m.f. measurements. Kohlrausch and Heydweiller* succeeded in measuring the conductance of ultra pure water. They obtained the lowest conductance ever recorded for pure water, *viz.*, 0.043×10^{-6} mho at 18°. This value was reached after forty-two back-and-forth distillations *in vacuo* at low temperatures. The glass conductance cell in which the measurement was made had been standing filled with water for 10 years. It is obvious that these precautions are essential, for the conductance of the water must be due entirely to hydrogen and hydroxyl ions if the dissociation constant of the water is to be calculated from conductance data. The method of calculating the dissociation constant is to calculate the concentration of the hydrogen and hydroxyl ions from the equation (see Chap. IV, Eq. 5)

$$\Lambda_0 = \frac{1{,}000\kappa_0}{c}. \tag{4}$$

The equivalent conductance Λ_0 is the sum of the limiting ionic conductances of the hydrogen and hydroxyl ions at 18°C., κ_0 is the specific conductance, and c is the concentration. From the table of mobilities given in Taylor's treatise,† Λ_0 is calculated to be 488 at 18°C. Kohlrausch and Heydweiller did not use their experimental value for the specific conductance of water in Eq. 4, however, but a slightly smaller value, 0.0377×10^{-6} mho; this last value was obtained by applying a correction to the value 0.043×10^{-6} mho for the error due to the dissolved impurities in the water which they were unable to eliminate. The amount of the impurity, approximately 0.00001 mg. in 15 cc., was estimated by comparing the temperature coefficient of conductance as experimentally found with the temperature coefficient calculated thermodynamically from the heat of dissociation of the water. The concentration of the ions in pure water is, therefore (at 18°C.),

* Kohlrausch, *Ann. Physik, Ergänzungsband,* **8**, 1, (1878); Kohlrausch and Heydweiller, *Ann. Physik,* **53**, 209 (1894); Kohlrausch, *Z. physik. Chem.,* **42**, 193 (1903); Heydweiller, *Ann. Physik,* (4) **28**, 503 (1909).

† "A Treatise on Physical Chemistry," Vol. I, p. 540, 1st ed., D. Van Nostrand Company, New York, 1924.

$$c = \frac{(1{,}000)(0.0377 \times 10^{-6})}{488}.$$
$$= 7.7 \times 10^{-8},$$

and K_w, the square of c, is, at 18°C., 0.59×10^{-14}. Heydweiller calculates K_w at 25°C. to be 1.04×10^{-14}. The dissociation constant, K_w, calculated by Heydweiller is the true dissociation constant given by Eq. (3) since the activity coefficients of the hydrogen and hydroxyl ion in pure water are equal to unity by definition.

The dissociation constant of water can also be calculated from e.m.f. measurements. It has already been shown in Chap. XVI how K_w has been calculated from the standard electrode potentials of the hydroxyl and hydrogen electrodes. The value obtained, 0.947×10^{-14} at 25°C. agrees closely with the value found by Heydweiller. Quite recently Bjerrum and Unmack and Harned and his coworkers have carried out extensive investigations on the dissociation of water in various salt solutions. Extrapolation to zero concentration yields the value of K_w. As an illustration of Harned's method we shall describe the work of Harned and Copson* on the dissociation of water in lithium chloride solutions. They measured the e.m.f. of the cells

$$\text{Pt, } H_2 \mid \text{LiOH } (0.01m), \text{ LiCl } (m) \mid \text{AgCl} \mid \text{Ag} \qquad (A)$$
$$\text{Pt, } H_2 \mid \text{HCl } (0.01m), \text{ LiCl } (m) \mid \text{AgCl} \mid \text{Ag} \qquad (B)$$

over the temperature range 15° to 35°C. and over the lithium chloride concentration range 0.01 to $5m$. The e.m.f. of cells of the type (A) is given by the equation

$$E_A = E^\circ - \frac{RT}{F} \ln \gamma_{H^+} \cdot \gamma_{Cl^-} \cdot m_{H^+} \cdot m_{Cl^-}. \qquad (5)$$

Using Harned and Copson's concentration units, the equation for the ionization constant of water becomes

* Harned and Schupp, *J. Am. Chem. Soc.*, **52**, 3892 (1930); Harned, *ibid.*, **47**, 930 (1925); Harned and Swindells, *ibid.*, **48**, 126 (1926); Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926); Harned and Mason, *J. Am. Chem. Soc.*, **54**, 3112 (1932); Harned and Hamer, *ibid.*, **55**, 2194 (1933). N. Bjerrum and Augusta Unmack, *Kgl. Danske Videnskab. Selskab., Math.-fys. Medd.*, **9**, 5 (1929). Harned and Copson, *J. Am. Chem. Soc.*, **55**, 2206 (1933).

$$K_w = \frac{\gamma_{H^+} \cdot \gamma_{OH^-}}{\gamma_{H_2O}} \cdot m_{H^+} \cdot m_{OH^-}. \tag{6}$$

In Eq. (6) it is necessary to introduce the activity coefficient of the water since the data cover the range of high concentrations. Eliminating m_{H^+} from Eqs. (6) and (5) and rearranging, we obtain

$$E_A - E^\circ + \frac{RT}{F} \ln \frac{m_{Cl^-}}{m_{OH^-}} = \frac{RT}{F} \ln \frac{\gamma_{H^+} \cdot \gamma_{OH^-}}{\gamma_{H_2O}} - \frac{RT}{F} \ln K_w - \frac{RT}{F} \ln \gamma_{H^+}\gamma_{Cl^-}. \tag{7}$$

At zero concentration the right-hand side of Eq. (7) equals $-RT/F \ln K_w$ since all the activity coefficients become equal to

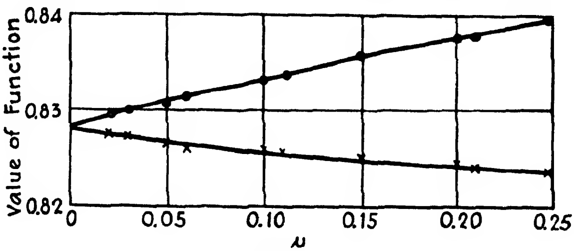

FIG. 1.

unity. By plotting the known values of the left-hand side of Eq. (7) against the ionic strength μ and by extrapolating to zero μ, $-RT/F \ln K_w$ is easily found. Such a plot is shown in Fig. 1, circles.

It is possible to treat the data in another way. Following the method of Harned and Hamer let the e.m.f. of cells (A) and (B) be represented by the equations

$$E_A = E^\circ - \frac{RT}{F} \ln m'_{H^+} \cdot m'_{Cl^-} \cdot \gamma'_{H^+} \cdot \gamma'_{Cl^-}. \tag{8}$$

$$E_B = E^\circ - \frac{RT}{F} \ln m''_{H^+} \cdot m''_{Cl^-} \cdot \gamma''_{H^+} \cdot \gamma''_{Cl^-}. \tag{9}$$

Subtracting,

$$E_A - E_B = \frac{RT}{F} \ln \frac{m''_{H^+} \cdot m''_{Cl^-} \cdot \gamma''_{H^+} \cdot \gamma''_{Cl^-}}{m'_{H^+} \cdot m'_{Cl^-} \cdot \gamma'_{H^+} \cdot \gamma'_{Cl^-}} = \frac{RT}{F} \ln \frac{m''_{H^+} \cdot m''_{Cl^-}}{m'_{H^+} \cdot m'_{Cl^-}}, \tag{10}$$

since $\gamma''_{H^+} \cdot \gamma''_{Cl^-}$ in the chloride-acid solutions equals very closely $\gamma'_{H^+} \cdot \gamma'_{Cl^-}$ in the chloride-hydroxide solutions because the acid

and hydroxide are at low concentration. Eliminating as before m'_{H^+} by means of Eq. (6), we obtain

$$E_A - E_B - \frac{RT}{F} \ln \frac{m''_{\text{H}^+} \cdot m''_{\text{Cl}^-} \cdot m'_{\text{OH}^-}}{m'_{\text{Cl}^-}} = \frac{RT}{F} \ln \frac{\gamma_{\text{H}^+} \cdot \gamma_{\text{OH}^-}}{\gamma_{\text{H}_2\text{O}}} - \frac{RT}{F} \ln K_w. \quad (11)$$

Harned and Hamer next replace

$$\ln \frac{\gamma_{\text{H}^+} \cdot \gamma_{\text{OH}^-}}{\gamma_{\text{H}_2\text{O}}}$$

by the expression

$$-\frac{2 \times 2.954 \times 10^6}{D^{3/2} T^{3/2}} \sqrt{2\mu} + \beta\mu,$$

which in part follows from the Debye and Hückel theory and in part is empirical. Their final equation is

$$E_A - E_B - \frac{RT}{F} \ln \frac{m''_{\text{H}^+} \cdot m''_{\text{Cl}^-} \cdot m'_{\text{OH}^-}}{m'_{\text{Cl}^-}} + \frac{RT}{F} \frac{5.908 \times 10^6}{D^{3/2} T^{3/2}} \sqrt{2\mu} = -\frac{RT}{F} \ln K_w + \frac{RT}{F} \beta\mu. \quad (12)$$

All activity coefficients have been eliminated from Eq. (12). By plotting known values of the left-hand side of Eq. (12) against the ionic strength, $-RT/F \ln K_w$ is readily obtained on extrapolation to zero concentration. This is an interesting extrapolation because the slopes of the curves are negative, Fig. 1 crosses, in contrast to the slopes of the curves of Eq. (7) which are positive. Such a double extrapolation to the same intercept is doubly reliable. Table I gives values for K_w over an extensive temperature range.

TABLE I.—THE DISSOCIATION CONSTANT OF WATER

$t°$ C.	0	5	10	15	20	25	30
$K_w \times 10^{14}$	0.115	0.186	0.293	0.452	0.681	1.008	1.471
$t°$ C.	35	40	45	50	55	60	
$K_w \times 10^{14}$	2.088	2.916	4.016	5.476	7.297	9.614	

Meaning of pH, pOH, pK.—At this point it should be pointed out that a convenient method of expressing very small or very

large numbers is provided by the "p" or negative logarithm system. This system, first introduced by Sørensen, arose because of the awkwardness in expressing by the usual methods the low values of the hydrogen ion concentration of biochemical and physiological solutions. In pure water, for example, the hydrogen ion concentration is 1×10^{-7} mole per liter. Since the pH is defined by the equation

$$\text{pH} = -\log m_{\text{H}^+} \cdot \gamma_{\text{H}^+}, \tag{13}$$

it is evident that the pH of pure water is +7. It is much easier to say or to write 7 than 1×10^{-7}. The pH is also equal to the negative of the exponent of the number 10 when the concentration is expressed as some power of 10. In 0.1 *N* sodium hydroxide the hydrogen ion concentration is approximately 1×10^{-13} and the pH is 13. Table II gives values of the hydrogen ion concentration and the approximate pH of the solution. If the activity coefficient of the hydrogen ion were known exactly, the exact pH could be calculated. In Chaps. XXIV and XXV methods for the experimental determination of the pH are described in detail. It should be noted that as the hydrogen ion concentration decreases the pH increases; the high pH values are, therefore, in alkaline solutions.

TABLE II.—APPROXIMATE RELATION BETWEEN pH AND CONCENTRATION

Solution	c_{H^+}	pH	pOH
8.0 *N* HCl	8	−1.17	15.17
1.0 *N* HCl	1	0	14
0.1 *N* HCl	1×10^{-1}	1	13
0.01 *N* HCl	1×10^{-2}	2	12
Pure water	1×10^{-7}	7	7
0.01 *N* NaOH	1×10^{-12}	12	2
1.0 *N* NaOH	1×10^{-14}	14	0

The pOH is defined by the equation

$$\text{pOH} = -\log m_{\text{OH}^-} \cdot \gamma_{\text{OH}^-}, \tag{14}$$

and the pK by the equation

$$\text{pK} = -\log \text{K}. \tag{15}$$

Since, for water (compare Eq. 6)

$$\log K_w = \log m_{H^+} \cdot \gamma_{H^+} + \log m_{OH^-} \cdot \gamma_{OH^-}, \tag{16}$$

it follows that

$$pK_w = pH + pOH. \tag{17}$$

Table II also includes values of pOH which are easily calculated from Eq. (17) since pK_w for water is 14 (at 25°C.).

Hydrolysis.—The value for the dissociation constant of water although small leads to an explanation of hydrolysis. Hydrolysis, illustrated by the reaction

$$NaOAc + H_2O \rightleftarrows HOAc + NaOH, \tag{18}$$

is defined as the reaction of a salt with water or sometimes as the reverse of neutralization.* It is with the ions of water, however, that the reaction is concerned, so that we can say that if water were not dissociated at all, hydrolysis would not occur. Hydrolysis is somewhat different depending on the nature of the salt. We can distinguish four types of salt, salts of a strong acid and weak base like ammonium chloride, salts of a strong base and weak acid like sodium acetate, salts of a weak base and weak acid like aniline acetate, and salts of a strong base and strong acid like sodium chloride. Let us consider salts of a strong acid and weak base. If the salt happens to be ammonium chloride, the following reactions will occur on adding the salt to water,

$$\begin{array}{ccc} NH_4Cl \rightarrow & NH_4^+ & + \; Cl^- \\ & + & \\ H_2O \rightleftarrows & OH^- & + \; H^+. \\ & \upharpoonleft\downharpoonright & \\ & NH_4OH & \end{array} \tag{19}$$

* In the following discussion of hydrolysis we shall limit the subject matter to the hydrolysis of salts of weak acids or weak bases whose dissociation constant is known. The reaction

$$SO_2Cl_2 + 2H_2O \rightarrow 2HCl + H_2SO_4$$

can be called an hydrolysis, but we shall not consider it as such here because according to our definition of hydrolysis given above we should have to consider sulfuric acid a very weak base which it obviously is not, and because equilibrium does not exist.

Since ammonium hydroxide is a weak base, its dissociation is governed by the L.M.A.

$$K_B = \frac{c_{NH_4^+} \cdot c_{OH^-}}{c_{NH_4OH}}. \tag{20}$$

This means that the ammonium ions which arise from the dissociation of the ammonium chloride must combine with the hydroxyl ion until the relationship expressed by Eq. (20) is fulfilled. As the hydroxyl ions are removed from the solution by the ammonium ions, more of the water molecules will dissociate producing more hydrogen and hydroxyl ions in the solution. Eventually the concentration of the hydrogen ions will be many times greater than the concentration of the hydroxyl ions and the solution will be, therefore, acid. However, the concentrations of the hydrogen and hydroxyl ions will always be of such magnitude to satisfy the equilibrium equation,

$$K_w = c_{H^+} \cdot c_{OH^-} \cdot f_{H^+} \cdot f_{OH^-}.$$

In the case of the hydrolysis represented by Eq. (19) the hydrogen and chloride ions do not combine because hydrochloric acid is a strong electrolyte, practically completely dissociated in water.

The hydrolysis may be made more complete if the product of the hydrolysis reaction is removed from the equilibrium either by precipitation or by volatilization. In the case of equilibrium (19) it is possible to increase the extent of hydrolysis by heating the solution; ammonia is more volatile than hydrogen chloride and escapes, leaving the solution definitely acid. The hydrolysis of ferric chloride, for example, is aided by the formation of the insoluble base, ferric hydroxide. Conversely the extent of hydrolysis is repressed by addition of either the free acid or free base formed in the hydrolysis.

The hydrolysis constant, K_h, is defined as the equilibrium constant of the reaction

$$NH_4^+ + Cl^- + H_2O \rightleftarrows NH_4OH + H^+ + Cl^-$$

in the case of the hydrolysis of a salt of a weak base and strong acid, the equilibrium constant being given by the equation (omitting activity coefficients)

$$K_h = \frac{c_{NH_4OH} \cdot c_{H^+} \cdot c_{Cl^-}}{c_{NH_4^+} \cdot c_{Cl^-}}. \tag{21}$$

The concentration of the water is omitted because it is practically a constant. Eliminating c_{H^+} by means of Eq. (3) we obtain

$$K_h = \frac{c_{NH_4OH} \cdot K_w}{c_{NH_4^+} \cdot c_{OH^-}}$$

or

$$K_h = \frac{K_w}{K_B}. \tag{22}$$

Equation (22) may be derived in another way. Let us consider the hydrolysis of a salt of weak base and strong acid. If c is the stoichiometric concentration of the salt, and if MOH represents the formula of the weak base formed by the hydrolysis and if x is the degree of hydrolysis or fraction of salt hydrolyzed, the following definitions may be set down:

$$c_{MOH} = cx, \tag{23a}$$
$$c_{M^+} = (1 - x)c, \tag{23b}$$

and

$$c_{H^+} = cx. \tag{23c}$$

The number of molecules of MOH formed is equal to the number of salt molecules hydrolyzed and since x is the fraction of salt molecules hydrolyzed, Eq. (23a) readily follows. The salt is assumed to be completely dissociated, so we can say that the concentration of the positive ion c_{M^+} is equal to $(1 - x)c$, Eq. (23b). Equation (23c) is based on the assumption that a hydrogen ion is produced for every molecule of base MOH formed; an assumption which is nearly valid due to the fact that the comparatively large concentration of the metal ion, c_{M^+}, represses the ionization of the base.

The dissociation constant for the base is defined by the relation (omitting activity coefficients)

$$K_B = \frac{c_{M^+} \cdot c_{OH^-}}{c_{MOH}}. \tag{24}$$

Replacing c_{OH^-} of Eq. (24) by means of the value of c_{OH^-} as given in Eq. (3) (again omitting activity coefficients), and rearranging, we obtain again the equation defining the hydrolysis constant K_h

$$K_h = \frac{c_{H^+} \cdot c_{MOH}}{c_{M^+}} = \frac{K_w}{K_B}. \tag{25}$$

An equation relating the degree of hydrolysis to the hydrolysis constant may be derived by replacing the quantities c_{H^+}, c_{MOH} and c_{M^+} by their values in terms of the degree of hydrolysis as given by Eqs. (23a), (23b), and (23c), *viz.*,

$$K_h = \frac{cx^2}{(1 - x)} \tag{26}$$

(compare this equation with the corresponding equation for the dissociation of an acid or base

$$K_c = \frac{c\alpha^2}{1 - \alpha}\Big).$$

Equation (26) may be solved for x, the result is

$$x = -\frac{K_h}{2c} + \sqrt{\frac{K_h^2}{4c^2} + \frac{K_h}{c}}. \tag{27}$$

If K_h/c is much less than unity, Eq. (27) may be simplified to

$$x = \sqrt{\frac{K_h}{c}}. \tag{28}$$

Equation (28) demonstrates that the degree of hydrolysis is roughly proportional to the square root of the hydrolysis constant and inversely proportional to the square root of the concentration. The more dilute the salt solution, the greater is the fraction of salt molecules hydrolyzed. Substituting the approximate Eq. (28) into Eq. (25),

$$x = \sqrt{\frac{K_w}{K_B c}}. \tag{29}$$

The weaker the base, therefore, the greater is the degree of hydrolysis. It is easy to derive an equation for the hydrogen ion concentration or pH of the salt solution by means of Eq. (29) remembering that $xc = c_{H^+}$

$$c_{H^+} = \sqrt{\frac{cK_w}{K_B}} \tag{30a}$$

or

$$\text{pH} = \tfrac{1}{2}\text{p}K_w - \tfrac{1}{2}\text{p}K_B - \tfrac{1}{2}\log c. \tag{30b}$$

The acidity of the salt solution, therefore, increases with increas-

ing salt concentration at the same time that the degree of hydrolysis is diminishing.

The hydrolysis of a salt of a weak acid and strong base can be represented by the equilibria, for example,

$$\begin{aligned} &\mathrm{NaOAc} \rightarrow \mathrm{Na^+} + \mathrm{OAc^-} \\ &\mathrm{H_2O} \rightleftarrows \mathrm{OH^-} + \mathrm{H^+} \\ &\qquad\qquad\qquad\quad \downarrow\uparrow \\ &\qquad\qquad\qquad\quad \mathrm{HOAc}. \end{aligned} \tag{31}$$

The equations for this hydrolysis reaction corresponding to Eqs. (25), (29), (30a), and (30b) are

$$K_h = \frac{c_{\mathrm{OH^-}} \cdot c_{\mathrm{HOAc}}}{c_{\mathrm{Ac^-}}} = \frac{K_w}{K_A} \tag{32a}$$

$$x = \sqrt{\frac{K_w}{cK_A}}, \tag{32b}$$

$$c_{\mathrm{H^+}} = \sqrt{\frac{K_w K_A}{c}} \tag{33a}$$

and

$$\mathrm{pH} = \tfrac{1}{2}\mathrm{p}K_w + \tfrac{1}{2}\mathrm{p}K_A + \tfrac{1}{2}\log c. \tag{33b}$$

Here, the hydrogen ion concentration decreases with rising salt concentration.

As examples of hydrolysis as a function of salt concentration and dissociation constant of acid Table III taken from Glasstone* may be quoted.

TABLE III.—DEGREES OF HYDROLYSIS FOR VARIOUS STRENGTHS OF ACID AND SALT CONCENTRATIONS (18°C.)

K_A	K_h	Salt concentration			
		0.001 N	0.01 N	0.1 N	N
10^{-4}	10^{-10}	3.3×10^{-4}	10^{-4}	3.2×10^{-5}	10^{-5}
10^{-6}	10^{-8}	3.2×10^{-3}	10^{-3}	3.2×10^{-4}	10^{-4}
10^{-8}	10^{-6}	0.032	0.01	3.2×10^{-3}	10^{-3}
10^{-10}	10^{-4}	0.27	0.095	0.032	10^{-2}

* S. GLASSTONE, "The Electrochemistry of Solutions," Methuen and Co., Ltd., London, 1930.

When the acid and base from which a salt is formed are both weak, the reaction of hydrolysis can be represented in the case of ammonium acetate, for example, by the following equilibria,

$$\begin{array}{ccccc} NH_4OAc \rightarrow & NH_4^+ & + & OAc^- & \\ & + & & + & \\ H_2O \rightleftarrows & OH^- & + & H^+ & \\ & \downarrow\uparrow & & \uparrow\downarrow & \\ & NH_4OH & & HOAc & \end{array} \tag{34}$$

If MOH and HA represent the weak base and weak acid, respectively, the following equations may be written down,*

$$K_w = c_{H^+} \cdot c_{OH^-} \tag{35}$$

$$K_A = \frac{c_{H^+} \cdot c_{A^-}}{c_{HA}}$$

$$K_B = \frac{c_{OH^-} \cdot c_{M^+}}{c_{MOH}}$$

and

$$K_h = \frac{K_w}{K_A \cdot K_B} = \frac{c_{HA} \cdot c_{MOH}}{c_{A^-} \cdot c_{M^+}}. \tag{36}$$

Equation (36) can also be derived by writing down the equilibrium constant K_h for the hydrolysis

$$M^+ + A^- + H_2O \rightleftarrows MOH + HA,$$

viz.,

$$K_h = \frac{c_{MOH} \cdot c_{HA}}{c_{M^+} \cdot c_{A^-}}.$$

The concentration of the water is omitted from this equilibrium constant equation since the concentration of the water is practically a constant, at least in dilute solutions.

If we regard both MOH and HA as being equally weak so that the same number of molecules of undissociated MOH and HA are formed, then it is true that

$$c_{MOH} = c_{HA} = cx \tag{37}$$

and

$$c_{A^-} = c_{M^+} = (1 - x)c. \tag{38}$$

* In all these equations activity coefficients have been omitted. One of the exercises at the end of the chapter is to derive certain of these equations taking into consideration the activity coefficients.

Eliminating c_{MOH}, c_{HA}, c_{A^-} and c_{M^+} from Eq. (36) by means of Eqs. (37) and (38), we obtain an equation for the hydrolysis constant in terms of x alone,

$$K_h = \frac{x^2}{(1-x)^2}. \tag{39}$$

A solution of a salt formed from an equally weak acid or base is neutral, that is, its pH is the same as pure water. This conclusion may be demonstrated as follows. From the dissociation equation for the acid

$$c_{H^+} = K_A \frac{c_{HA}}{c_{A^-}}. \tag{40}$$

Introducing Eqs. (37) and (38) into (40),

$$c_{H^+} = K_A \cdot \frac{x}{1-x}, \tag{41}$$

but from Eq. (39)

$$\sqrt{K_h} = \frac{x}{1-x},$$

and from Eq. (36)

$$K_h = \frac{K_w}{K_A \cdot K_B};$$

hence

$$c_{H^+} = K_A\sqrt{K_h} = \sqrt{\frac{K_A K_w}{K_B}}, \tag{42}$$

or

$$\mathrm{pH} = \tfrac{1}{2}\mathrm{p}K_A + \tfrac{1}{2}\mathrm{p}K_w - \tfrac{1}{2}\mathrm{p}K_B. \tag{43}$$

If

$$K_A = K_B,$$
$$\mathrm{pH} = \tfrac{1}{2}\mathrm{p}K_w$$

or

$$c_{H^+} = 1 \times 10^{-7}.$$

If

$$K_A > K_B$$
$$c_{H^+} > 1 \times 10^{-7}$$

and the solution is acidic. If

$$K_A < K_B$$
$$c_{H^+} < 1 \times 10^{-7}$$

and the solution is basic.

Experimental Determination of Hydrolysis.—The degree of hydrolysis may be determined by either a conductance or e.m.f.

method. Other methods have been invented, but as they are not electrochemical methods, they will not be described here. Bredig* developed the following conductance method in measuring the hydrolysis of aniline hydrochloride. Aniline hydrochloride is the salt of a weak base and strong acid; in solutions of this salt there will be $(1 - x)$ equivalents of unhydrolyzed salt per stoichiometric equivalent of salt, and x equivalents of acid and base formed in the hydrolysis. The base, in the case of aniline hydrochloride, is weak and practically completely undissociated; hence it will not contribute to the electrical conductance of the solution. The equivalent conductance Λ of the solution as a whole can be expressed by the equation

$$\Lambda = (1 - x)\Lambda_{AH^+} + (1 - x)\Lambda_{Cl^-} + x\Lambda_{H^+} + x\Lambda_{Cl^-}. \tag{44}$$

In Eq. (44) Λ_{AH^+} represents the equivalent conductance of the $C_6H_5NH_3^+$ ion. Solving Eq. (44) for x, we get

$$x = \frac{\Lambda - \Lambda_{AH^+} - \Lambda_{Cl^-}}{\Lambda_{H^+} - \Lambda_{AH^+}}. \tag{45}$$

In Eq. (45) Λ is the measured conductance, Λ_{H^+} and Λ_{Cl^-} can be estimated from known conductances of the hydrogen and chloride ions at different salt concentrations, but Λ_{AH^+} must be found by additional measurements. Bredig determined Λ_{AH^+} by adding to the salt solution free aniline until the conductance became constant. The added aniline is supposed to repress the hydrolysis, and not to affect the conductance itself. When hydrolysis has been practically completely prevented by the addition of the aniline, the conductance of the solution should be solely due to that of the salt, aniline hydrochloride.† Bredig's aniline hydrochloride data are given in Table IV.

The conductance values of the third and fourth columns of Table IV are the equivalent conductances of the salt solution plus $\frac{1}{64}$ mole of free aniline per liter, and $\frac{1}{32}$ mole of free aniline per liter, respectively. Since there is not much difference between these two columns, the hydrolysis is evidently practically completely repressed at the free aniline concentration of $\frac{1}{64}$ mole per liter. It is interesting to note that the conductance of the

* BREDIG, *Z. physik. Chem.*, **191**, 213, 289, 321 (1894).

† This treatment follows closely the discussion given by Glasstone, *op. cit.*, p. 172.

solution is appreciably lowered by the addition of the aniline. The calculated hydrolysis constants are reasonably constant over the range of concentration studied.

TABLE IV.—EQUIVALENT CONDUCTANCES OF ANILINE HYDROCHLORIDE SOLUTIONS AND DEGREES OF HYDROLYSIS

$1/c$	Λ	Λ_B ($c_B = 1/64$)	Λ_B ($c_B = 1/32$	x	$K_h \times 10^5$
64	106.2	96.0	95.9	0.036	2.1
128	113.7	98.2	98.1	0.055	2.5
256	122.0	100.3	100.1	0.077	2.5
512	131.8	101.5	101.4	0.109	2.6
1024	144.0	103.3	103.3	0.147	2.5

The e.m.f. method for determining the extent of hydrolysis consists in measuring the hydrogen ion concentration of the solution or the pH, by methods which will be described in Chaps. XXIV and XXV. As an example of this method the experiments of Čupr* who recently measured the degree of hydrolysis of zinc sulfate solutions at various concentrations may be cited. The degree of hydrolysis in this case may be defined as

$$x = \frac{c_{H^+}}{c}, \tag{46}$$

where c_{H^+} is the concentration of hydrogen ions in the solution resulting from the hydrolysis of the zinc sulfate and c is the stoichiometrical concentration of the zinc sulfate. Čupr measured the pH of a 0.1c solution of zinc sulfate by means of the quinhydrone electrode and found it to be 5.34. This gives a hydrogen ion concentration of 4.6×10^{-6} if one wishes to neglect the activity coefficient of the hydrogen ion and the liquid-junction potential existing between the quinhydrone electrode and the reference electrode. The degree of hydrolysis is, therefore (in per cent)

$$x = \frac{4.6 \times 10^{-6}}{0.1} \cdot 100 = 0.0046,$$

This is the figure obtained by Čupr.

* V. ČUPR, *Z. anorg. allgem. Chem.*, **198**, 310 (1931).

Ampholytes.—Every freshman student of chemistry becomes familiar with amphoteric hydroxides such as zinc hydroxide. Zinc hydroxide is capable of acting either as base or acid according to the equilibria,

$$2H^+ + ZnO_2^= \rightleftarrows H_2ZnO_2 \rightleftarrows Zn(OH)_2 \rightleftarrows Zn^{++} + 2OH^-.$$

Addition of acid to zinc hydroxide removes the hydroxyl group from its equilibrium causing the above reaction to proceed to the right and resulting in the formation of zinc chloride, zinc sulfate, etc. Addition of base to zinc hydroxide removes the hydrogen ion from the above equilibrium causing the reaction to run to the left and resulting in the formation of sodium, potassium, etc., zincate. In organic chemistry we have the amino acids of the type

$$NH_2RCOOH$$

acting as amphoteric substances which we may call ampholytes. According to classical concepts amino acids could exist in aqueous solutions in three forms, as a cation

$$^+NH_3RCOOH,$$

as a neutral molecule,

$$NH_2RCOOH,$$

and as an anion,

$$NH_2RCOO^-.$$

The amphion,

$$^+NH_3RCOO^-,$$

was not considered to exist in appreciable quantities. Küster* gave the German name, "Zwitterion," to the above ion, but Adams and Bjerrum† stated that the amphion was an important constituent of solutions of amino acids. Bjerrum's argument in favor of the amphion is based on the fact that if the acidic and basic dissociation constants of the ampholyte are calculated according to the classical interpretation of the dissociation of ampholytes, *i.e.*, by the equations (letting brackets denote concentrations),

* Küster, *Z. anorg. allgem. Chem.*, **13**, 135 (1897).

† N. Bjerrum, *Z. physik. Chem.*, **104**, 147 (1923); E. Q. Adams, *J. Am. Chem. Soc.*, **38**, 1503 (1916). See also Cohn, *Erg. d. Physiol.*, **33**, 781 (1931).

$$K'_A = \frac{[H^+][NH_2RCOO^-]}{[NH_2RCOOH]} \tag{47}$$

and

$$K'_B = \frac{[OH^-][^+NH_3RCOOH]}{[NH_2RCOOH]}, \tag{48}$$

values of K'_A and K'_B result which are unreasonable; whereas if the acid and base constants are calculated according to the assumption of the existence of the amphion, much more plausible values of the dissociation constants are obtained. As an illustration of this argument let us consider the dissociation constants of glycine,

$$NH_2CH_2COOH.$$

The older ideas give

$$K'_A = \frac{[H^+][NH_2CH_2COO^-]}{[NH_2CH_2COOH]} = 1.8 \times 10^{-10} \tag{49}$$

and

$$K'_B = \frac{[OH^-][NH_3^+CH_2COOH]}{[NH_2CH_2COOH]} = 2.7 \times 10^{-12}. \tag{50}$$

The dissociation constants of acetic acid and ammonia, chemically similar substances, are approximately equal to 1×10^{-5}. This value is not even of the same order of magnitude as the acid and base dissociation constants of glycine as calculated by Eqs. (47) and (48). According to Bjerrum, the dissociation of glycine is to be represented not by the equations,

$$NH_2CH_2COOH \rightleftarrows NH_2CH_2COO^- + H^+ \tag{51a}$$
$$NH_2CH_2COOH + H_2O \rightleftarrows NH_3^+CH_2COOH + OH^-, \tag{51b}$$

but by the equations

$$NH_3^+CH_2COOH \rightleftarrows NH_3^+CH_2COO^- + H^+ \tag{52a}$$
$$NH_2CH_2COO^- + H_2O \rightleftarrows NH_3^+CH_2COO^- + OH^-. \tag{52b}$$

Equations (51*a*) and (52*b*) should be compared as well as equations (51*b*) and (52*a*). In this comparison set NH_2CH_2COOH equal to $NH_3^+CH_2COO^-$. The acid and base dissociation constants for equations (52) are

$$K_A = \frac{[H^+][NH_3^+CH_2COO^-]}{[NH_3^+CH_2COOH]} \tag{53a}$$

and

$$K_B = \frac{[OH^-][NH_3^+CH_2COO^-]}{[NH_2CH_2COO^-]}. \tag{53b}$$

Bjerrum also shows that K_A and K_B are related to K'_A and K'_B by the equations

$$K_A = \frac{K_w}{K'_B} \tag{54a}$$

$$K_B = \frac{K_w}{K'_A}, \tag{54b}$$

since the amphion, $NH_3^+CH_2COO^-$, according to Bjerrum's hypothesis, is to be conceived as the same as the neutral molecule NH_2CH_2COOH of the older ideas. The new values of K_A and K_B are 4.7×10^{-3} and 7.1×10^{-5}. These values are much more reasonable since they are approximately of the same order of magnitude as the dissociation constants of ammonia and acetic acid. [Compare Eqs. (54a) and (54b) with Eqs. (25) and (32a).]

Harned and Owen* have reported preliminary values for the acid and base constants of glycine obtained from cells without liquid junctions. They also calculate the activity coefficient of the glycine base defined as

$$\gamma_B = \sqrt{\frac{\gamma_{Z\pm} \cdot \gamma_{OH^-}}{\gamma_{G^-} \cdot \gamma_{H_2O}}} \tag{55}$$

where $\gamma_{Z\pm}$ is the activity coefficient of the amphion,

$$NH_3^+CH_2COO^-,$$

and γ_{G^-} is the activity coefficient of the ion, $NH_2CH_2COO^-$. According to modern theories of electrolytes the activity coefficient of the base would be expected to vary linearly with the ionic strength of the solution since Eq. (55) contains the activity coefficients of negative ions in both the numerator and denominator. The interionic attraction effects would thereby tend to cancel out of Eq. (55). Scatchard and Kirkwood† also have shown theoretically that the logarithm of the activity coefficient of the amphion varies in dilute solution linearly with the ionic strength and not with the square root of the ionic strength.

* H. S. Harned and B. B. Owen, *J. Am. Chem. Soc.*, **52**, 5091 (1930).

† G. Scatchard and J. G. Kirkwood, *Physik. Z.*, **33**, 297 (1932).

Hence we should expect that a plot of log γ_B or log γ_A against the ionic strength would result in a straight line. Harned and Owen actually find this to be the case.

The dielectric properties of amphions are interesting as indeed might be expected considering the large separation of the positive and negative charges in the amphion molecule. It is found rather surprisingly that the dielectric constant of solutions of amphions in various solvents increases linearly with the concentration. This fact is illustrated in Fig. 2 where the dielectric constants of aqueous solutions of glycine at 25°C. are plotted as a function of the concentration.* Even up to the high concentration of 2.5 moles per liter the linear function is verified. Wyman and McMeekin find that the slopes of the dielectric constant-concentration curves are identical or practically so for the same ampholyte dissolved in different solvents, that for aqueous solutions the slopes of ampholytes of the same type are nearly all the same, and that the slopes increase regularly as the separation between the acidic and basic groups in the molecule increases. The interpretation of these interesting facts is not yet entirely clear, but enough is known for the conclusion to be reached that the Clausius-Mosotti expression (see Chap. XII) is not applicable.

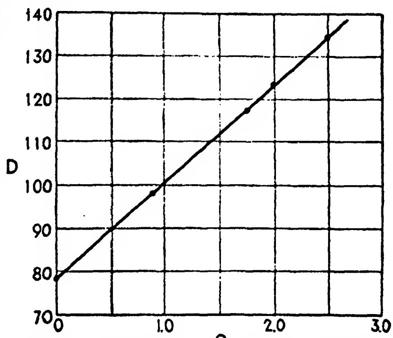

FIG. 2.—Dielectric constant of glycine solutions.

Buffer Solutions.—The existence of weak acids and bases makes possible the formation of the so-called buffer solutions, which are of great importance biologically and technically. Phosphoric acid in combination with its salts forms perhaps the most widely used system of buffer solutions. The dissociation of phosphoric acid may be represented by the equations,

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^- \tag{56a}$$
$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^= \tag{56b}$$
$$HPO_4^= \rightleftarrows H^+ + PO_4^{\equiv}. \tag{56c}$$

* See J. WYMAN, JR. *J. Am. Chem. Soc.*, **56**, 536 (1934).
WYMAN and McMEEKIN, *ibid.*, **55**, 908 (1933).

From the data in Table V, Chap. XX, we learn that the first dissociation constant of phosphoric acid (the equilibrium constant for reaction (56*a*)) is 8.30×10^{-3}. From the table of dissociation constants collected by Clark* the equilibrium constants for dissociations (56*b*) and (56*c*) are 6.9×10^{-8} and 2.2×10^{-13}, respectively. Thus we find that $HPO_4^{=}$ is an exceedingly weak acid. If some sodium phosphate is added to a solution of phosphoric acid, the concentration of phosphate ions is greatly increased since we may regard sodium phosphate as being completely dissociated. The addition of the phosphate ions reduces the concentration of the hydrogen ions due to formation of the weakly dissociated acids, $HPO_4^{=}$ and $H_2PO_4^{-}$. The resulting mixture of phosphoric acid and sodium phosphate is known as a buffer solution, because the hydrogen ion concentration of the solution is changed with difficulty. If a base such as sodium hydroxide is added to the solution, the hydrogen ion concentration is not materially reduced at first due to the buffering action of the weak acids, $HPO_4^{=}$ and $H_2PO_4^{-}$. As the hydrogen ions are removed by the base to form water, more hydrogen ions appear due to the dissociation of $HPO_4^{=}$ and $H_2PO_4^{-}$ so that the hydrogen ion concentration remains nearly constant. Conversely, if hydrochloric acid is added to the solution, the hydrogen ions from the hydrochloric acid combine with the phosphate ions to form the undissociated $HPO_4^{=}$ and $H_2PO_4^{-}$, so that once more the hydrogen ion concentration remains practically constant. This behavior is clearly illustrated in Table V which is taken from Clark's book, p. 216. As the sodium hydroxide is added the hydrogen ion concentration changes very slowly.

TABLE V.—VARIATION OF pH OF Na_2HPO_4 SOLUTION ON ADDITION OF SODIUM HYDROXIDE

Mixture (diluted to 50 cc.)	pH
25 cc. *A* 4.13 cc. *B*	11.00
25 cc. *A* 6.00 cc. *B*	11.20
25 cc. *A* 8.67 cc. *B*	11.40
25 cc. *A* 12.25 cc. *B*	11.60
25 cc. *A* 16.65 cc. *B*	11.80
25 cc. *A* 21.60 cc. *B*	12.00

Solution *A*: 17.81 g. of $Na_2HPO_4.2H_2O$ per liter.
Solution *B*: 0.1 *N* NaOH.

* W. M. CLARK, "The Determination of Hydrogen Ions," 3d ed., p. 678, Williams & Wilkins Company, Baltimore, 1928.

Buffer solutions are important biologically, because they maintain the pH of biological fluids approximately constant. Blood is a fluid whose pH is maintained with remarkable constancy usually between the limits 7.3 and 7.5 by means of the bicarbonate-carbonic acid equilibrium and the protein systems in the blood. It would be extremely difficult if not impossible to control the pH of an unbuffered solution such as a solution of sodium chloride within a narrow pH range.

The platinum type of hydrogen electrode cannot be used to determine the pH of unbuffered solutions, but it gives accurate, reproducible and constant values in the present of buffered solutions.

Exercises

1. Derive Eqs. (32*a*) and (33*b*).
2. Derive Eqs. (25) and (36) including the activity coefficients. Predict roughly the variation of K_h of Eq. (25) and K_h of Eq. (36) with increasing salt concentration.
3. K_A for acetic acid is 1.8×10^{-5}. Calculate the degree of hydrolysis of 0.1 N sodium acetate.

CHAPTER XXII

PHASE-BOUNDARY AND SEMIPERMEABLE-MEMBRANE POTENTIALS

Definition of Phase-boundary Potentials.—The existence of phase-boundary or interfacial potentials is one of the most universal facts of nature. Wherever we have two immiscible phases in contact, we can be sure that an interfacial potential exists. This is particularly important for biological systems where electric potentials across cell walls or cell membranes are always present. A measurement of these biological potentials often gives clues to interesting physiological phenomena which might have escaped attention if the electrical potentials could not have been observed.* It is known that electric potentials exist in the human body, even persisting for several hours after clinical death. Unfortunately, as we shall see later, the measurement of these potentials is never completely free from ambiguity. Nevertheless the study of phase-boundary and semipermeable-membrane potentials is interesting and important.

What do we mean by a phase-boundary potential? Fundamentally, the potential at the surface of a metal dipping into a solution of its ions is a phase-boundary potential, because the metal constitutes one phase and the solution another. However, the metal-solution potentials are not generally referred to as phase-boundary potentials; this name is usually restricted to the potentials that exist between phases in which the electrical conduction is electrolytic and not electronic. Thus, an interfacial potential between a water phase and an oil phase is a phase-boundary potential, a potential between an insoluble solid such as mercurous chloride and a solution is a phase-boundary potential; potentials between two insoluble solids, between a solid and a gas, and between a liquid and a gas are also phase-boundary potentials.

* See, for example, W. J. V. Osterhout, *J. Gen. Physiol.*, **11**, 83 (1927).

The definition of a phase-boundary potential is based upon the existence of chemical, thermal, and mechanical equilibrium between the two phases in contact. For example, let us consider the phase-boundary potential that exists between an aqueous solution of hydrochloric acid and a solution of hydrogen chloride in benzene, Fig. 1.

The original hydrochloric acid concentration is immaterial; on shaking up the benzene with the water, hydrogen chloride will pass from the water into the benzene until equilibrium is attained. On closing the circuit by connecting the two hydrogen electrodes together it is found that the e.m.f. is zero and that no current flows through the cell. If the hydrogen chloride is not distributed according to the equilibrium conditions, a current will flow transporting hydrogen chloride in the correct direction until equilibrium exists. The current will then become equal to zero and the net e.m.f. must be equal to zero, for the thermodynamic definition of equilibrium is that dG, and hence dE, are equal to zero. The interfacial potential, ψ_p, that exists after equilibrium is established at the junction of the water and benzene phases is defined as the phase-boundary potential.

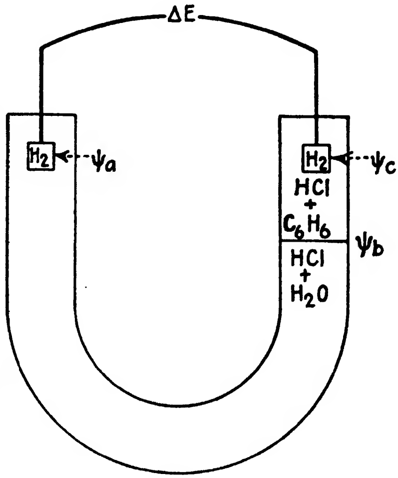

FIG. 1.

Let us represent the cell as pictured in Fig. 1 by the symbols

$$\begin{array}{c}\text{Pt, } H_2 \mid \ HCl' \ \mid \ HCl'' \ \mid H_2\text{, Pt.} \\ a \ (H_2O) \ b \ (C_6H_6) c\end{array}$$

Since the total e.m.f. of the cell is zero, neither the right-hand, nor the left-hand electrode is the positive electrode, so it is immaterial in what order we write down the cell. However, it is possible that a potential will exist at the two metal-solution junctions a and c and also at the phase boundary b. Denoting an interfacial potential by the symbol ψ, the e.m.f. of the cell will be given by the equation

$$\psi_a + \psi_b + \psi_c = 0. \tag{1}$$

If the two potentials at the hydrogen electrodes oppose each other equally (the cell is so arranged that the hydrogen electrodes do oppose each other), the phase-boundary potential will be equal to zero. It is possible to prove that in general this will never be true: we can conclude, therefore, that a phase-boundary potential does actually exist.

Before considering the general thermodynamic treatment of phase-boundary potentials, it is interesting to point out that if the absolute single-electrode potentials could be measured experimentally, the phase-boundary potentials could be calculated unambiguously. Thus, if ψ_a and ψ_c could be separately determined, it would be an easy matter to calculate the phase-boundary potential from Eq. (1). The whole problem of phase-boundary potentials can be reduced in this way to the problem of determining the absolute value of a single-electrode potential. Since we know nothing definite concerning the latter, we know nothing definite concerning the boundary potential between two phases.

Thermodynamics of Phase-boundary Potentials.—In Chap. XV it was demonstrated by Gibbs's method that whenever we have two or more phases in contact and in equilibrium the chemical potentials μ of each individual substance present must be the same everywhere throughout the system. When aqueous hydrochloric acid is shaken up with benzene, both water and hydrogen chloride dissolve in the benzene phase until their chemical potentials are equal in the two phases and benzene dissolves in the aqueous phase until the chemical potential of the benzene is the same in the water solution as it is in the benzene solution. If the benzene phase is denoted by double primes and the aqueous phase by single primes, the following equations may be written down:

$$\mu'_{H_2O} = \mu''_{H_2O} \tag{2a}$$

$$\mu'_{HCl} = \mu''_{HCl} \tag{2b}$$

and

$$\mu'_{C_6H} = \mu''_{C_6H_6}. \tag{2c}$$

These equations are valid at equilibrium irrespective of the hydrochloric acid concentration or the temperature.

In Chap. XVI it was demonstrated that the e.m.f. of a cell is due to the difference in chemical potentials of the reacting substances; when the chemical potentials are everywhere equal the e.m.f. is zero. In the case of phase boundaries the chemical potential of the hydrochloric acid has the same value throughout the heterogeneous system, hence we can ask ourselves why should a phase-boundary potential exist. The answer to this question lies in a consideration of the chemical potentials of the *ions.* If the chemical potential of the hydrogen ion is the same in both the water and benzene phases (Fig. 1), the phase-boundary potential will be equal to zero because the potentials at the electrodes ψ'_{H^+} and ψ''_{H^+} will be equal and opposite. Since the total e.m.f. is zero, the phase-boundary potential would have to be equal to zero. But we know that the chemical potential of the hydrogen ion is probably not the same in the two phases; therefore, we know that there must be a phase-boundary potential. This last statement cannot be rigorously proved unless one restricts oneself to such dilute solutions that the activity coefficient can be set equal to unity. However, if it is true for dilute solutions, it is reasonable to assume that it is also true for concentrated solutions.

To prove that the hydrogen ion cannot possibly have the same chemical potential in the two phases let us start with the necessary assumption that the solutions are so dilute that the activity coefficient of the hydrogen ion is equal to unity in each phase. Then

$$\mu'_{H^+} = RT \ln c'_{H^+} + \mu^{\circ\prime}_{H^+} \tag{3a}$$

and

$$\mu''_{H^+} = RT \ln c''_{H^+} + \mu^{\circ\prime\prime}_{H^+}. \tag{3b}$$

Let us now calculate the value of $\psi'_{H^+} + \psi''_{H^+}$ since if we can prove that the sum of the two electrode potentials is not equal to zero, we can prove that a phase-boundary potential must exist. Imagine one faraday of electricity to flow reversibly through the cell represented by Fig. 1 so that hydrogen ions move in the direction of phase (′) to phase (″); *i.e.*, from the water to the benzene. The reaction at the hydrogen electrode in the aqueous phase is

$$\tfrac{1}{2}H_2 \rightarrow H^+(') + \epsilon^-$$

and the net change in chemical potential is

$$\Delta\mu_1 = \mu'_{H^+} - \tfrac{1}{2}\mu_{H_2} + \mu_{\epsilon^-}. \tag{4}$$

The reaction at the hydrogen electrode in the benzene phase is

$$\epsilon^- + H^+('') \rightarrow \tfrac{1}{2}H_2$$

with a change in chemical potential given by the equation

$$\Delta\mu_2 = \tfrac{1}{2}\mu_{H_2} - \mu''_{H^+} - \mu_{\epsilon^-}. \tag{5}$$

Since

$$\Delta\mu_1 = -nF\psi'_{H^+} \tag{6a}$$

and

$$\Delta\mu_2 = -nF\psi''_{H^+}, \tag{6b}$$

it follows that

$$nF(\psi'_{H^+} + \psi''_{H^+}) = \mu''_{H^+} - \mu'_{H^+} \tag{7}$$

or on eliminating μ''_{H^+} and μ'_{H^+} by means of Eqs. (3)

$$\psi'_{H^+} + \psi''_{H^+} = \frac{RT}{nF} \ln \frac{c''_{H^+}}{c'_{H^+}} + \frac{1}{nF}(\mu^{\circ\,\prime\prime}_{H^+} - \mu^{\circ\,\prime}_{H^+}). \tag{8}$$

In order that $\psi' + \psi''$ be equal to zero (we are attempting to prove that this is not the case), it is necessary that

$$\frac{RT}{nF} \ln \frac{c''_{H^+}}{c'_{H^+}} = -\frac{1}{nF}(\mu^{\circ\,\prime\prime}_{H} - \mu^{\circ\,\prime}_{H^+}) \tag{9}$$

or simply that

$$\frac{c''_{H^+}}{c'_{H^+}} = K_{H^+}, \tag{10}$$

where K_{H^+} is a constant, the ordinary distribution coefficient. If the cell of Fig. 1 had contained chlorine electrodes instead of hydrogen electrodes, we could equally well have derived the equation

$$\frac{c''_{Cl^-}}{c'_{Cl^-}} = K_{Cl^-}. \tag{11}$$

Now it follows absolutely that c'_{H^+} must equal c'_{Cl^-}, c''_{H^+} must equal c''_{Cl^-} and K_{H^+} must equal K_{Cl^-} because both phases must remain *electrically neutral.* By a similar line of reasoning we can prove that all ions would have the same distribution coefficient and since these distribution coefficients are also the distribution coefficients for the salts of the ions (in these dilute solutions the

dissociation may be assumed to be complete), it is necessary for all salts to have the same distribution coefficients if the sum of the two electrode potentials $\psi_i' + \psi_i''$ is equal to zero. But we know that all salts do not have the same distribution coefficient, therefore, we know that $\psi_i' + \psi_i''$ will not be equal to zero, and consequently that a phase-boundary potential must exist. The reason for this is clear; it is necessary that the hydrogen ion diffuse freely and independently of the chloride ion between the two phases for μ_{H^+}' to equal μ_{H^+}'' or for $\psi_{H^+}' + \psi_{H^+}''$ to equal zero, but the hydrogen ion in the system of Fig. 1 cannot distribute itself freely between the two phases. Every time that a hydrogen ion diffuses from the water to the benzene it must carry a chloride ion along with it in order to maintain the electroneutrality of the phases. The necessary simultaneous migration of both the positive and negative ions can be thought of as an *electrical restriction* acting on the hydrogen ion which makes it impossible for the chemical potential of the hydrogen ion to become equal in the two phases. Of course, a very small number of excess hydrogen or chloride ions may diffuse, but it is just this excess that gives rise to the boundary potential. When we come to the study of semipermeable-membrane potentials, we shall see that in this case a *mechanical* restriction prevents the free diffusion of the ions and thus gives rise to a membrane potential.

Although we do not have chemical equilibrium in regard to the ions, we do have a certain type of equilibrium which Guggenheim calls electrochemical equilibrium. Guggenheim* states that whenever two phases are brought into contact the electrochemical potential $\bar{\mu}$ of any ion is the same in the two phases. Thus, for the cell represented in Fig. 1 we can say that

$$\bar{\mu}_{H^+}' = \bar{\mu}_{H^+}'', \tag{12}$$

and

$$\mu_{Cl^-}'' = \bar{\mu}_{Cl^-}'. \tag{13}$$

For the hydrogen ion the electrochemical potential is defined as the chemical potential plus the electrostatic potential of the solution ψ; for the aqueous phase, for example

$$\bar{\mu}_{H^+}' = \mu_{H^+}' + F\psi' \tag{14a}$$

* E. A. Guggenheim, *J. Phys. Chem.*, **33**, 842 (1929); **34**, 1540 (1930); Brønsted, *Z. physik. Chem.*, **143**, 301 (1929).

and

$$\bar{\mu}'_{\mathrm{Cl}^-} = \mu'_{\mathrm{Cl}^-} - F\psi'. \tag{14b}$$

(Since $n = 1$, here). For the benzene phase we have the similar relations,

$$\bar{\mu}''_{\mathrm{H}^+} = \mu''_{\mathrm{H}^+} + F\psi'' \tag{15a}$$

and

$$\bar{\mu}''_{\mathrm{Cl}^-} = \mu''_{\mathrm{Cl}^-} - F\psi''. \tag{15b}$$

The phase-boundary potential $(\psi'' - \psi')$ depends, therefore, upon the difference in the chemical potentials of the ions,

$$\mu'_{\mathrm{H}^+} - \mu''_{\mathrm{H}^+} = F(\psi'' - \psi') \tag{16a}$$

and

$$\mu'_{\mathrm{Cl}^-} - \mu''_{\mathrm{Cl}^-} = -F(\psi'' - \psi'). \tag{16b}$$

Eliminating the chemical potentials by means of the equation,

$$\mu_i = \mu_i^\circ + RT \ln c_i\mathbf{f}_i,$$

we obtain the relations,

$$\psi_p = \psi'' - \psi' = \frac{1}{F}(\mu^{\circ\prime}_{\mathrm{H}^+} - \mu^{\circ\prime\prime}_{\mathrm{H}^+}) + \frac{RT}{F} \ln \frac{c'_{\mathrm{H}^+} \cdot \mathbf{f}'_{\mathrm{H}^+}}{c''_{\mathrm{H}^+} \cdot \mathbf{f}''_{\mathrm{H}^+}} \tag{17*}$$

and

$$\psi_p = \psi'' - \psi' = \frac{1}{F}(\mu^{\circ\prime\prime}_{\mathrm{Cl}^-} - \mu^{\circ\prime}_{\mathrm{Cl}^-}) + \frac{RT}{F} \ln \frac{c''_{\mathrm{Cl}^-} \cdot \mathbf{f}''_{\mathrm{Cl}^-}}{c'_{\mathrm{Cl}^-} \cdot \mathbf{f}'_{\mathrm{Cl}^-}} \tag{18}$$

Guggenheim concludes that a single-phase-boundary potential or a single-electrode potential has no physical significance because it cannot be defined in terms of physically measurable quantities. We cannot measure the potential at a single interface and we cannot calculate it from an equation like Eq. (18) because we know nothing concerning the value of $\mu^{\circ\prime\prime}_{\mathrm{Cl}^-} - \mu^{\circ\prime}_{\mathrm{Cl}^-}$, or of ionic activity coefficients.

However, just as we can measure the difference in potential between two metallic electrodes we can measure the difference in

* We are defining the phase-boundary potential as being equal to $\psi'' - \psi'$ because this definition results in a potential which opposes the two potentials of the electrodes; in other words, relation (1) must be satisfied. By adding Eq. (17) to Eq. (8) it is readily seen that the sum of all the potentials in the cell of Fig. 1 is zero. Equation (17) could have been derived in the same way that Eq. (8) was derived by considering the change in chemical potential of the hydrogen and chloride ions when positive current flows to the right, let us say.

potential between two phase boundaries. Consider the following cell illustrated in Fig. 2,

			a	b	c	d	e			
Hg	HgCl	sat. KCl	HCl in H_2O c'	HCl in C_6H_6 c''	HNO_3 in C_6H_6 c'''	HNO_3 in H_2O c''''	sat. KCl	HgCl	Hg	(A)

In writing down cell (A) a single vertical line represents a phase boundary while a double vertical line indicates a liquid junction between two solutions having the same solvent. The potentials

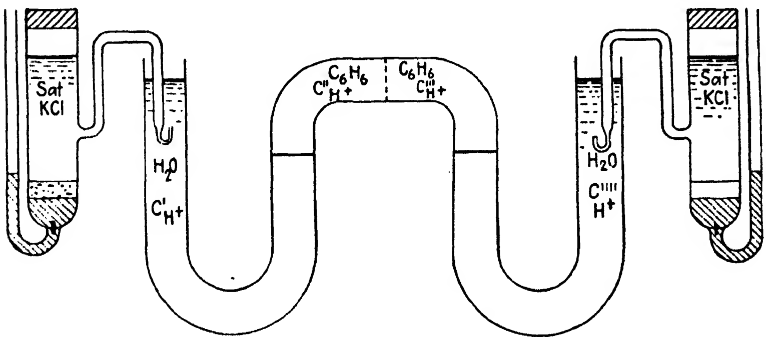

FIG. 2.

of the calomel electrodes balance out, and the liquid-junction potentials, at a, c, and e are so small that they may be neglected. The phase-boundary potentials at b and d are given by the following equations [from Eq. (17)]

$$\psi_b = \frac{RT}{F} \ln \frac{c'_{H^+}f'_{H^+}}{c''_{H^+}f''_{H^+}} + \frac{1}{F}(\mu^{\circ\prime}_{H^+} - \mu^{\circ\prime\prime}_{H^+}) \tag{19}$$

and

$$\psi_d = \frac{RT}{F} \ln \frac{c'''_{H^+}f'''_{H^+}}{c''''_{H^+}f''''_{H^+}} + \frac{1}{F}(\mu^{\circ\prime\prime}_{H^+} - \mu^{\circ\prime}_{H^+}), \tag{20}$$

since $\mu^{\circ\prime\prime}_{H^+} = \mu^{\circ\prime\prime\prime}_{H^+}$ and $\mu^{\circ\prime}_{H^+} = \mu^{\circ\prime\prime\prime\prime}_{H^+}$.
The net e.m.f. of the cell is found by adding Eqs. (19) and (20), obtaining thereby

$$E = \psi_b + \psi_d = \frac{RT}{F} \ln \frac{c'_{H^+}f'_{H^+}c'''_{H^+}f'''_{H^+}}{c''_{H^+}f''_{H^+}c''''_{H^+}f''''_{H^+}}. \tag{21}$$

If we assume that the activity coefficients are equal in the separate phases, we can write Eq. (21)

$$E = \psi_b + \psi_d = \frac{RT}{F} \ln \frac{c'_{H^+} c'''_{H^+}}{c''_{H^+} c''''_{H^+}}. \tag{22}$$

Equation (22) contains measurable quantities, providing we assume one hundred per cent dissociation. If we make the hydrogen ion concentration the same in the two aqueous phases, Eq. (22) reduces to

$$E = \frac{RT}{F} \ln \frac{c'''_{H^+}}{c''_{H^+}}. \tag{23}$$

Of course, the cell of Fig. 2 may be varied in a number of ways; some of these variations will be described in the next section. Before considering the experimental results, it is well to list the assumptions that have been made by scientists in their use of equations similar to Eqs. (22) and (23).

1. All liquid-junction potentials have been neglected.
2. Ionic-activity coefficients have been assumed to be equal to unity or to be constant.
3. Ionic concentrations have been assumed equal to the stoichiometrical concentration (100 per cent dissociation) or have been calculated roughly from conductance measurements.
4. Thermodynamic equilibrium has been assumed to exist at the phase boundaries, although we know that equilibrium does not exist in the interior of a phase. Thus in cell (A) no diffusion potential would be present at c if complete equilibrium is established. However, in order to measure any e.m.f. we cannot allow complete equilibrium to be established.

Despite these assumptions the experimental data are interesting and important.

Experimental Data for Phase-boundary Potentials between Immiscible Liquids.—Beutner* is chiefly responsible for what little information we have concerning phase-boundary potentials. He made many measurements on all types of cells including such interesting physiological systems as an apple, one-half of

* R. Beutner, *J. Am. Chem. Soc.*, **35**, 344 (1913); **36**, 2040, 2045 (1914). "Die Enstehung elektrischer Ströme in lebenden Geweben." (Inaugural Dissertation of Reinhard Beutner, Friedrich-Wilhelms Universität.) Ferdinand Enke, Stuttgart, **1920.** See also L. Michaelis, "Hydrogen Ion Concentration," Chap. VIII, Williams & Wilkins Company, Baltimore, 1926.

an apple, one-third of an apple, and the skin of an apple. Two typical cells of Beutner from which several important conclusions were drawn are

(−)					(+)
Calomel	0.2 c sodium salicylate in H_2O c'	1.0 c dimethyl toluidine salicylate in nitrobenzene c''	0.1 c dimethyl toluidine salicylate in nitrobenzene c'''	0.2 c sodium salicylate in H_2O c'	Calomel (*B*)

Observed e.m.f. of *B* equaled 0.031 v.

(−)					(+)
Calomel	0.2 c dimethyl toluidine hydrochloride in H_2O c'	0.1 c dimethyl toluidine salicylate in nitrobenzene c''	1.0 c dimethyl toluidine salicylate in nitrobenzene c'''	0.2 c dimethyl toluidine hydrochloride in H_2O c'	Calomel (*C*)

Observed e.m.f. of *C* equaled 0.035 v.

In cells (*B*) and (*C*) the saturated potassium chloride bridge and saturated calomel electrode are abbreviated to calomel. These cells are of the same type of cell (*A*); the salicylate ion is the common ion in cell (*B*), and the equation for the e.m.f. is

$$E_B = \frac{RT}{F} \ln \frac{c'' \text{ salicylate}}{c''' \text{ salicylate}}, \qquad c'' > c'''. \tag{24}$$

In cell (*C*), dimethyl toluidine ion is the common ion, and the equation for the e.m.f. is

$$E_C = \frac{RT}{F} \ln \frac{c''' \text{ dimethyl toluidine}}{c'' \text{ dimethyl toluidine}}, \qquad c'' < c'''. \tag{25}$$

However, one should not expect that the concentrations to use in Eqs. (24) and (25) are the stoichiometrical concentrations in the nitrobenzene, because on bringing the aqueous solution and the nitrobenzene solution into contact, the concentrations right at the phase boundaries must be changed by diffusion in order to bring about equilibrium at these two points. If one does calculate the e.m.f. of cells (*B*) and (*C*) using the stoichiometrical concentration, the value of 0.059 v. results, whereas the observed e.m.f. is only 0.031 v. in cell (*B*) and 0.035 v. in cell (*C*). The

interesting conclusion can be drawn, however, that the diffusion potential in the nitrobenzene has very little to do with the e.m.f.; for in cell (*B*) the e.m.f. is 0.031 v. and in cell (*C*) the e.m.f. is −0.035 v. (taking the e.m.f. of both cells in the same direction). If the diffusion potential in the nitrobenzene contributed the major part of the observed e.m.f., it would be impossible to change the sign of the e.m.f. by changing the composition of the aqueous solutions.

Beutner points out that the sign for the observed e.m.f. depends upon the common ion. Thus, in cell (*B*) the common ion is the salicylate ion, and since its most concentrated nitrobenzene layer is at the left of cell (*B*), the left-hand side of cell (*B*) is negative. In cell (*C*), the dimethyl toluidine ion is the common ion, so that cell (*C*) will be positive on the end in which the nitrobenzene has the greater concentration of these ions. Beutner says that cells (*B*) and (*C*) would be equivalent to ordinary concentration cells with liquid junctions if the aqueous solutions were replaced by metallic electrodes.

Beutner measured the e.m.f. of a similar cell in which he determined the concentration of the oily phases after equilibrium had been established, and in this way he was able to calculate the e.m.f. theoretically. He shook up some guaiacol with a 0.1 *c* aqueous solution of sodium chloride and another portion of guaiacol with a 0.1 *c* aqueous solution of dimethyl aniline hydrochloride. Using these solutions he measured the e.m.f. of the following cell

(−)					(+)
Calomel	0.1 *c* dimethyl aniline hydrochloride in H_2O	dimethyl aniline hydrochloride in guaiacol	sodium chloride in guaiacol	0.1 *c* sodium chloride in H_2O	Calomel (*D*)
	c'	c''	c'''	c'	

Observed e.m.f. = 0.091 v.

The common ion is the chloride ion; hence the equation for the e.m.f. is

$$E_D = \frac{RT}{F} \ln \frac{c''_{Cl^-}}{c'''_{Cl^-}}. \tag{26}$$

Beutner measured the conductance of the two guaiacol solutions

and found that the dimethyl aniline hydrochloride guaiacol solution had a conductance 58.9/1.1 times as great as the sodium chloride guaiacol solution. Making the assumption that this conductance ratio is equal to the concentration ratio, c''_{Cl^-}/c'''_{Cl^-}, Beutner calculated the e.m.f. to be 0.1 v. Since the observed figure was 0.091 v., the agreement is very good, but considering the assumptions involved, the agreement must be thought rather fortuitous. Beutner obtained, however, similar agreement with a number of other cells employing guaiacol and *p*-cresol as the oily solvents.

A surprising fact concerning phase-boundary potentials is the effect of the chemical nature of the oily phase upon the magnitude of the observed e.m.f. Beutner studied concentration cells of the type

(−)				(+)
Calomel	0.1 c KCl in H_2O	salicylic aldehyde saturated with salicylic acid	$\frac{c}{6,250}$ KCl in H_2O	Calomel (*E*)

and

Calomel	0.1 c KCl in H_2O	benzyl alcohol	$\frac{c}{6,250}$ KCl in H_2O	Calomel. (*F*)
		a	*b*	

Cell (*E*) gave an e.m.f. of 0.125 v., while cell (*F*) gave an e.m.f. of zero! Beutner explains this remarkable difference in behavior by assuming that in cell (*E*) the following reaction takes place:

$$\underset{\text{salicylic acid}}{C_7H_5O_3H} + KCl \rightleftarrows C_7H_5O_3K + HCl.$$

As potassium chloride diffuses into or out of the oily phase the above reaction runs to the right as written or to the left with the net result that the concentration of the potassium chloride in the oily phase remains practically constant. Such a reaction can take place because hydrochloric acid is a weak acid in the nonaqueous solvent, salicylic aldehyde. In the case of cell (*F*), benzyl alcohol is an inert solvent and does not react with the potassium chloride; hence the concentration of potassium chloride will not remain constant but will vary in accordance with its distribution ratio. If the potassium chloride is distributed according to its distribution ratio

$$\frac{c'_{KCl}}{c''_{KCl}} = K \tag{27}$$

at both boundaries the interfacial potential at the phase boundaries, a and b of cell (F), will be given by the identical equations (with signs opposite)

$$E_a = \frac{RT}{F} \ln K$$

$$E_b = -\frac{RT}{F} \ln K, \tag{28}$$

hence the sum of the potentials is equal to zero. In the case of cell (E), the chemical reaction prevents the potassium chloride from distributing itself according to its distribution ratio so that an e.m.f. results.

Beutner also measured the e.m.f. of cells which might be considered to be analogous to ordinary e.m.f. cells without liquid junction. Combining together cells (B) and (C), Beutner obtained the cell (G)

(−)						(+)
Calomel	0.2 c sodium salicylate in H_2O	1.0 c dimethyl toluidine salicylate in nitrobenzene	0.2 c dimethyl toluidine hydrochloride in H_2O	0.1 c dimethyl toluidine salicylate in nitrobenzene	0.2 c Na salicylate in H_2O	Calomel (G)

The liquid-junction potentials between the calomel half cells and the aqueous solutions balance out. By remembering that the aqueous phases are considered by Beutner to be analogous to metal electrodes, it is readily seen why cell (G) may be called a concentration cell without a liquid junction. The e.m.f. of cell (G), 0.066 v., is exactly equal to the sum of cells (B) and (C). It is not assumed, however, that all diffusion potentials have been eliminated from cell (G).

It is possible to arrange cells in which the aqueous phases have no ion in common, as

Calomel	0.1 c Na_2SO_4 in H_2O	toluidine	0.1 c KCl, in H_2O	Calomel	(H)

for which Beutner measured a potential of 0.120 v.

Although in none of the cells described could it be said that equilibrium had been established in accordance with our original

definition of phase-boundary potentials, nevertheless Beutner's work is important. In the words of Michaelis, "These relationships represent perhaps some of the most important recent advances in physiological physics, for here we have succeeded for the first time in obtaining electromotive forces of the order of magnitude of those observed physiologically, without the participation of free metals." Beutner was thus able to give a possible explanation for some of the bio-electric phenomena previously observed.

In the discussion of the glass electrode, Chap. XXIX, phase-boundary potentials will be treated from a statistical mechanical viewpoint; perhaps all phase-boundary potentials will be so interpreted in the future.

Attention should also be called to the work of Farkas* who quotes an unpublished equation derived by Debye for the potential of a phase boundary, *viz.*,

$$\psi_p = \frac{\epsilon}{2}\left(\frac{1}{r_-} - \frac{1}{r_+}\right)\left(\frac{1}{D_{\text{oil}}} - \frac{1}{D_{H_2O}}\right).$$

In this equation ψ_p is the potential at the phase boundary, ϵ is the unit electrical charge, r_- and r_+ are the radii of the negative and positive ions, respectively. D_{oil} is the dielectric constant of the oily phase after it has been saturated with water and D_{H_2O} is the dielectric constant of the water phase after it has been saturated with oil. The difficulty in testing Debye's equation rests in the lack of information as to the actual values of r_- and r_+, to say nothing of the uncertainty involved in the experimental determination of ψ_p.

Semipermeable-membrane Potentials.—In our discussion of phase-boundary potentials it was stated that an electrical restriction existed which prevented any one ion from distributing itself freely between two phases independently of any other ion. Suppose that two aqueous solutions of hydrochloric acid of different concentrations are separated by a membrane permeable only to hydrogen ions as in Fig. 3.

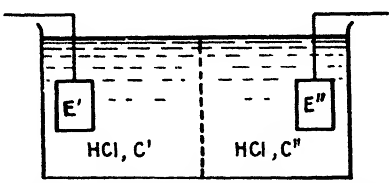

FIG. 3.—Hydrochloric acid concentration cell with membrane permeable only to hydrogen ions.

* P. Farkas, *Z. Elektrochem.*, **38**, 654 (1932).

Hydrogen ions will tend to diffuse through the membrane from the more concentrated solution (c'') to the more dilute (c'), but very few if any hydrogen ions will so diffuse because chloride ions are prevented by the *mechanical* restriction from penetrating through the membrane, and unless chloride ions can diffuse, hydrogen ions will be unable to do so since each solution must remain electrically neutral. In other words, a hydrogen ion must take a chloride ion along with it in order to get through the membrane. However, when the current passes, hydrogen ions will pass through the boundary at the rate of one equivalent of hydrogen per faraday of electricity. Faraday's second law of electrolysis is as exactly fulfilled for the membrane as it is for the metallic electrodes.

If the two hydrogen electrodes, E' and E'', are connected together, current will flow until equilibrium exists and the net e.m.f. becomes equal to zero. Since the potential at the two electrodes is given by the equation [compare Eq. (8)]

$$\psi'_{H^+} + \psi''_{H^+} = \frac{RT}{F} \ln \frac{c''_{H^+} \cdot f''_{H^+}}{c'_{H^+} \cdot f'_{H^+}},$$

the potential at the membrane must be equal to [compare Eq. (17)]

$$\psi_m = \frac{-RT}{F} \ln \frac{c''_{H^+} \cdot f''_{H^+}}{c'_{H^+} \cdot f'_{H^+}}. \tag{29}$$

This potential could be easily measured by means of the cell

$$(+) \quad \text{Calomel} \left\| \begin{matrix} \text{HCl} \\ c' \end{matrix} \right| \text{membrane} \left| \begin{matrix} \text{HCl} \\ c'' \end{matrix} \right\| \text{Calomel} \ (-) \qquad (I)$$

$$(c'' > c')$$

provided we neglect diffusion potentials between the hydrochloric acid solutions and the potassium chloride salt bridge of the two calomel half cells.

Equation (29) may also be derived thermodynamically. When equilibrium exists,

$$\bar{\mu}'_{H^+} = \bar{\mu}''_{H^+};$$

i.e., the hydrogen ions are in electrochemical equilibrium on both sides of the membrane. But

$$\begin{aligned} \bar{\mu}'_{H^+} &= \mu'_{H^+} + F\psi' = \bar{\mu}''_{H^+} = \mu''_{H^+} + F\psi'' \\ (\psi'' - \psi')F &= (\mu' - \mu'') \\ &= RT \ln c'_{H^+} \cdot f'_{H^+} + \mu^\circ_{H^+} - RT \ln c''_{H^+} \cdot f''_{H^+} - \mu^\circ_{H^+}. \end{aligned}$$

The constants cancel, hence

$$\psi_m = \frac{RT}{F} \ln \frac{c'_{H^+} \cdot f'_{H^+}}{c''_{H^+} \cdot f''_{H^+}}$$

in agreement with Eq. (29).

Although Gibbs had at an early date worked out the fundamental thermodynamics applicable to semipermeable membranes, it was Donnan who made an extensive study of membrane equilibria and potentials; hence the equations and relations go under the general name of Gibbs-Donnan membrane equations.* Donnan and Green† studied cells similar to cell (*I*) in which the potassium ion was the permeable ion and obtained results in substantial agreement with Eq. (29).

Suppose a cell is constructed of a hydrochloric acid solution separated by a membrane from a sodium chloride solution and let us assume that the membrane is permeable to both hydrogen and sodium ions (Fig. 4). It is now possible for hydrogen ions to diffuse through the membrane from one solution to the other provided sodium ions diffuse in the opposite direction. The electroneutrality of the solution will thus be maintained. At equilibrium both solutions will contain hydrogen and sodium ions. If the solution c'' is more concentrated with respect to chloride ions, it will contain more of both hydrogen and sodium ions; in fact, the ratio $\frac{c''_{H^+}f''_{H^+}}{c'_{H^+}f'_{H^+}}$ must equal the ratio $\frac{c''_{Na^+}f''_{Na^+}}{c'_{Na^+}f'_{Na^+}}$ at equilibrium because the phase-boundary potential must equal the difference in electrode potentials irrespective of the particular electrodes used, *i.e.*, whether the electrodes are hydrogen or sodium electrodes. The equality of these ratios may also be deduced from the following reasoning: At equilibrium the exchange of a hydrogen ion in solution (c'') for a sodium ion in

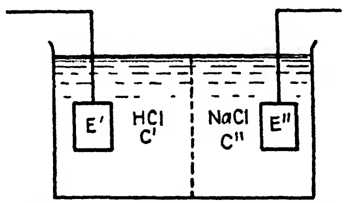

FIG. 4.—Semipermeable-membrane cell, membrane permeable to both hydrogen and sodium ions. (Before equilibrium.)

* See F. G. Donnan, *Chem. Rev.*, **1**, 73 (1924) for a general review of semipermeable-membrane equilibria and potentials. For a recent extended treatment see Donnan, *Z. physik. Chem.*, **A 168**, 369 (1934).

† F. G. DONNAN and G. GREEN, *Proc. Roy. Soc.*, **A 90**, 450 (1914).

solution (c') must result in a zero change of free energy (the definition of equilibrium). The free-energy change in this transfer will only be zero when $\frac{c''_{H^+}f''_{H^+}}{c'_{H^+}f'_{H^+}}$ equals $\frac{c''_{Na^+}f''_{Na^+}}{c'_{Na^+}f'_{Na^+}}$ for the work done by the system on the migration of the hydrogen ion per gram equivalent is $RT \ln \frac{c''_{H^+} \cdot f''_{H^+}}{c'_{H^+} \cdot f'_{H^+}}$ and the work done on the system by the migration of the sodium ion per gram equivalent is $-RT \ln \frac{c''_{Na^+} \cdot f''_{Na^+}}{c'_{Na^+} \cdot f'_{Na^+}}$. The total work must add up to zero.

The membrane potential is given by the equation

$$\psi_m = -\frac{RT}{F} \ln \frac{c''_{H^+} \cdot f''_{H^+}}{c'_{H^+} \cdot f'_{H^+}} = -\frac{RT}{F} \ln \frac{c''_{Na^+} \cdot f''_{Na^+}}{c'_{Na^+} \cdot f'_{Na^+}}. \tag{30}$$

A situation of more widespread occurrence than either of the above two cases is represented in Fig. 5. R represents some organic cation of such large size that it is unable to penetrate the membrane. The sodium and chloride ions readily diffuse through the membrane. Since both the sodium and the chloride ions can diffuse until equilibrium is attained, it is possible to write down the equilibrium condition of Gibbs

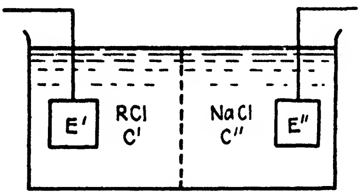

FIG. 5.—Semipermeable-membrane cell with membrane permeable to all but one ion. (Before equilibrium.)

$$\mu'_{NaCl} = \mu''_{NaCl}, \qquad \text{or} \qquad \mu'_{Na^+} + \mu'_{Cl^-} = \mu''_{Na^+} + \mu''_{Cl^-}. \tag{31}$$

It should be noted that here we can have equality between the chemical potentials, but if we are dealing solely with ions, we can only speak of equality between the electrochemical potentials. Since the chemical potentials are equal on both sides of the membrane, the products $c_i f_i$ must also be equal; so we can write

$$c'_{NaCl} \cdot f'_{NaCl} = c''_{NaCl} \cdot f''_{NaCl} \tag{32}$$

or

$$c'_{Na^+} \cdot f'_{Na^+} \cdot c'_{Cl^-} \cdot f'_{Cl^-} = c''_{Na^+} \cdot f''_{Na^+} \cdot c''_{Cl^-} \cdot f''_{Cl^-}$$

or

$$\frac{c''_{Cl^-} \cdot f''_{Cl^-}}{c'_{Cl^-} \cdot f'_{Cl^-}} = \frac{c'_{Na^+} \cdot f'_{Na^+}}{c''_{Na^+} \cdot f''_{Na^+}}. \tag{33}$$

From a consideration of electrode and membrane potentials we could also arrive at the relationship expressed by Eq. (33).

Gillespie* gives a concise and general equation for the membrane potential, *viz.*,

$$\psi_m = \frac{RT}{F} \ln \left(\frac{c_i' \mathrm{f}_i'}{c_i'' \mathrm{f}_i''}\right)^{\frac{1}{z_i}} \qquad c_i'' \mathrm{f}_i'' > c_i' \mathrm{f}_i', \tag{34}$$

where c_i' and c_i'' are the concentrations of the diffusable ion in the two solutions [Eq. (34) can be applied to any diffusable ion] f_i' and f_i'' the ionic-activity coefficients, z_i is the valence of the ion, negative when negative.

In this brief discussion of semipermeable-membrane potentials, nothing has been said of the possible diffusion of neutral water molecules or of the hydrogen or hydroxyl ions that are present in the solution due to the dissociation of water molecules. In acid solutions we can neglect the hydroxyl ion and in neutral solutions the effect of the hydrogen and hydroxyl ions upon the potential is only infinitesimal. However, hydrogen ions will diffuse until the $c_{H^+} \cdot \mathrm{f}_{H^+}$ ratio is given by Eq. (34). This means that we can calculate the membrane potential by measuring the so-called pH of both solutions. If the Nf product or the chemical potential of water is the same on both sides of the membrane, we can neglect the migration of water.

An interesting subject which has not yet been investigated is the semipermeable-membrane potential across the membrane before equilibrium has been attained. Similarly, no one has yet investigated the phase-boundary potential between two phases at the moment of contact.

We also need to know more concerning a possible connection between phase-boundary potentials and semipermeable-membrane potentials. Thus, it is possible that the existence of a large phase-boundary potential is due to the selective permeability of the phase boundary to one particular ion. In this connection see the discussion of the glass electrode in Chap. XXV.

Phase-boundary Potentials between a Solid and a Liquid.—Hitherto in this book we have often dealt with electrodes of the type

$$\mathrm{Hg} \mid \mathrm{HgCl} \mid \text{solution},$$

* L. J. Gillespie, "Physical Chemistry," p. 236. McGraw-Hill Book Company, Inc., New York, 1931.

but we have not studied the potential that exists at the phase boundary

$$HgCl \mid \text{solution}.$$

Haber* was the first to investigate the e.m.f. of cells such as

$$Hg \mid HgCl \quad \mid 1\ c\ KCl \mid HgCl \quad \mid 1\ c\ HgNO_3 \| 1\ c\ KCl \mid HgCl \mid Hg. \qquad (J)$$

On varying the concentration of the mercurous nitrate solution, the e.m.f. of the cell varied approximately in accordance with the equation

$$E = \frac{RT}{nF} \ln \frac{c''_{HgNO_3} \cdot f''_{HgNO_3}}{c'_{HgNO_3} \cdot f'_{HgNO_3}}. \tag{35}$$

At the surface of the mercurous nitrate and mercurous chloride, electrochemical equilibrium exists between mercurous ions in solution and in the solid; hence it is easy to derive Eq. (35) in the same way that previous equations in this chapter have been derived.

Other interesting boundaries are those between aqueous solutions and the following substances; glass, quartz, paraffin, graphite, and carborundum. These boundaries will not be considered here except the boundary glass-aqueous solution. This last boundary constitutes the "glass electrode," and as several fundamental principles of electrochemistry are illustrated by the glass electrode, it will be discussed in Chap. XXV.

Exercises

1. Derive the equation for the net e.m.f. of the cell

$$Hg \left| HgCl \right| \begin{matrix}\text{sat.}\\ KCl\end{matrix} \left\| \begin{matrix}0.1\ N\\ CH_3COOH\end{matrix} \right| \begin{matrix}\text{membrane}\\ \text{permeable}\\ \text{to } H^+ \text{ ions}\end{matrix} \left| \begin{matrix}0.2\ N\\ CH_3COOH\end{matrix} \right\| \begin{matrix}\text{sat.}\\ KCl\end{matrix} \left| HgCl \right| Hg.$$

2. Enough hydrochloric acid is added to the two acetic acid solutions of the cell in Exercise 1 to make both solutions 1.0 N in hydrochloric acid. Assuming that the total volume of each solution is the same as in Exercise 1, and that the membrane is also permeable to the chloride ion describe all the concentration changes that take place.

3. Derive two different equations for the e.m.f. of the resulting cell in Exercise 2.

4. Derive an exact thermodynamic equation for the e.m.f. of the cell

$$Ba, Hg \left| \begin{matrix}0.1\ N\\ BaCl_2\end{matrix} \right| \begin{matrix}\text{membrane}\\ \text{permeable to}\\ \text{chloride ions}\end{matrix} \left| \begin{matrix}0.01\ N\\ BaCl_2\end{matrix} \right| Ba, Hg.$$

5. Derive Eq. (29) from a consideration of the cell reactions when the current flows.

* F. Haber, *Ann. Physik*, (4), **26**, 927 (1908).

CHAPTER XXIII

OXIDATION AND REDUCTION CELLS

An important class of cells with liquid junction is the type which goes under the name of oxidation and reduction cells. These cells are particularly interesting to the bacteriologist and biologist, because oxidation and reduction processes such as respiration and assimilation play an exceedingly important role in nature. Oxidation and reduction cells are also of great interest to the organic chemist as is evidenced by the research work which is now going on in this field. The analytical chemist makes frequent use of oxidimetric potentiometric titrations and in the field of general inorganic chemistry a knowledge of oxidation-reduction or "redox" potentials is helpful in understanding and classifying many inorganic reactions.

Oxidation originally referred to the simple addition of oxygen to a substance, but this definition is too restricted for modern chemistry because there are numerous oxidation reactions in which oxygen does not enter. For example, we say that ethyl alcohol is oxidized to acetaldehyde in the reaction

$$CH_3CH_2OH + \tfrac{1}{2}O_2 \rightarrow CH_3CHO + H_2O,$$

but the alcohol gains no oxygen, it is the two hydrogens in the compound that have been oxidized to water. The oxidation of the ethyl alcohol really consists in the loss of two hydrogens. Similarly, we should consider ethylene as being the oxidation product of ethane. The oxidation of cuprous ions to cupric in the reaction $Cu^+ + Fe^{+++} \rightarrow Cu^{++} + Fe^{++}$ involves no oxygen, nor does the reaction $Fe^{++} + \tfrac{1}{2}Cl_2 \rightarrow Fe^{+++} + Cl^-$. Oxidation in these reactions means the loss of an electron or the gain in positive valence. As a complete definition of oxidation we shall have to say that it includes (1) the addition of oxygen, (2) the loss of hydrogen, and (3) the loss of electrons. Conversely reduction is the loss of oxygen, the gain of hydrogen or the gain of electrons.

Not all oxidation processes can be studied electrochemically, however; perhaps it is better to define oxidation and reduction as being simply the loss or gain of electrons, respectively. Perhaps we should exclude oxygenation and hydrogenation reactions from the general class of oxidation and reduction reactions. Practically we shall have to do so, for it is impossible, for example, to study potentiometrically the hemoglobin-oxyhemoglobin system. The formation of oxyhemoglobin from hemoglobin seems to be merely the addition of molecular oxygen to hemoglobin rather than a true oxidation-reduction process.*

Oxidation and reduction reactions are of interest to electrochemists due to the fact that an inert or "unattackable" electrode

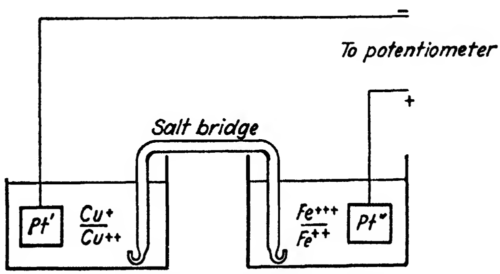

FIG. 1.—A typical oxidation-reduction cell.

such as gold or platinum develops a characteristic potential when immersed in a solution containing oxidizing or reducing agents. From the observed e.m.f. we can calculate the free energy or driving force of the reaction and the equilibrium constant in exactly the same way as with an ordinary galvanic cell. A typical redox cell is illustrated in Fig. 1 in which the reaction as the current flows is $Cu^+ + Fe^{+++} \rightarrow Fe^{++} + Cu^{++}$. Ferric ions take up one electron each at the right-hand or positive electrode to become ferrous ions, while cuprous ions give up one electron each on the negative electrode to become cupric ions. In accordance with our convention positive electricity flows from left to right through the cell. This tendency of ferric ions to take on an electron and of cuprous ions to give off an electron produces a definite e.m.f. which is a measure of the free energy of the reaction.†

* J. B. CONANT, *J. Biol. Chem.*, **27**, 401 (1923).

† In this discussion of oxidation-reduction potentials we shall assume that

Equations for the Oxidation-reduction Potentials.—In the early days of electrochemistry it was thought unnecessary to include the ferrous and cupric ion concentrations in describing the cell; it was not known that a change of concentration of these ions changed the observed e.m.f. However, Peters* in 1898 pointed out that whenever there are any Fe^{+++} ions, there must be some Fe^{++} ions for a stable potential to exist and that the equation for the potential at a single electrode is given by the general equation

$$E = \mathbf{E}^{\circ}_{ox.\rightarrow red.} + \frac{RT}{nF} \ln \frac{c_{ox.}}{c_{red.}}, \tag{1}$$

where $c_{ox.}$ and $c_{red.}$ represent the concentrations of the oxidant (oxidized form) and reductant (reduced form), respectively.

The derivation of Eq. (1) and similar redox e.m.f. equations may be illustrated in the case of the cell

$$\text{Pt} \mid \text{Cu}^{++}, \text{Cu}^{+} \parallel \text{salt bridge} \parallel \text{Fe}^{+++}, \text{Fe}^{++} \mid \text{Pt} \tag{A}$$

whose cell reaction is

$$\text{Cu}^{+} + \text{Fe}^{+++} \rightarrow \text{Cu}^{++} + \text{Fe}^{++}. \tag{2}$$

Considering the cuprous-cupric electrode, we have the electrode reaction as one faraday of electricity flows through the cell

$$\text{Cu}^{+} \rightarrow \text{Cu}^{++} + \epsilon^{-}, \tag{3}$$

with a change in chemical potential

$$\Delta\mu_1 = \mu_{\text{Cu}^{++}} + \mu_{\epsilon^-} - \mu_{\text{Cu}^{+}}. \tag{4}$$

At the ferric-ferrous electrode, the reaction per faraday

$$\text{Fe}^{+++} + \epsilon^{-} \rightarrow \text{Fe}^{++} \tag{5}$$

occurs with a change in chemical potential

$$\Delta\mu_2 = \mu_{\text{Fe}^{++}} - \mu_{\text{Fe}^{+++}} - \mu_{\epsilon^-}. \tag{6}$$

Adding Eqs. (4) and (6) (omitting from consideration the reactions at the liquid junction),

$$\Delta\mu = \mu_{\text{Cu}^{++}} + \mu_{\text{Fe}^{++}} - \mu_{\text{Cu}^{+}} - \mu_{\text{Fe}^{+++}}; \tag{7}$$

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the salt bridge reduces the liquid-junction potential to a negligible quantity. Activity coefficients will usually be neglected. Very little is known concerning activity coefficients of oxidizing and reducing ions.

* R. Peters, *Z. physik. Chem.*, **26** 193, (1898).

and introducing concentrations, activity coefficients, and the e.m.f.

$$E = \mathbf{E}^\circ_{Fe^{+++}\rightarrow Fe^{++}} - \mathbf{E}^\circ_{Cu^{++}\rightarrow Cu^{+}} + \frac{RT}{F} \ln \frac{c_{Cu^+}\mathbf{f}_{Cu^+}c_{Fe^{+++}}\mathbf{f}_{Fe^{+++}}}{c_{Cu^{++}}\mathbf{f}_{Cu^{++}}c_{Fe^{++}}\mathbf{f}_{Fe^{++}}} \qquad (8)$$

which is Eq. (1) applied to cell (A).

It is obvious from Eq. (8) that a measurement of the e.m.f. of cell (A) will tell us nothing about the ratio of concentrations of the ions entering into the reaction unless the standard electrode potentials of the two electrodes,

$$\mathbf{E}^\circ_{Cu^{++}\rightarrow Cu^{+}} \quad \text{and} \quad \mathbf{E}^\circ_{Fe^{+++}\rightarrow Fe^{++}}$$

are known. From a consideration of the reactions at either of the single electrodes, we can derive the equations for the single-electrode potentials from Eqs. (4) and (6)*

$$E_{Cu^{+}\rightarrow Cu^{++}} = -\mathbf{E}_{Cu^{++}\rightarrow Cu^{+}} + \frac{RT}{F} \ln \frac{c_{Cu^+}\mathbf{f}_{Cu^+}}{c_{Cu^{++}}\mathbf{f}_{Cu^{++}}}, \qquad (9)$$

and

$$E_{Fe^{+++}\rightarrow Fe^{++}} = \mathbf{E}^\circ_{Fe^{+++}\rightarrow Fe^{++}} + \frac{RT}{F} \ln \frac{c_{Fe^{+++}}\mathbf{f}_{Fe^{+++}}}{c_{Fe^{++}}\mathbf{f}_{Fe^{++}}}. \qquad (10)$$

Since

$$E = E_{Cu^{+}\rightarrow Cu^{++}} + E_{Fe^{+++}\rightarrow Fe^{++}}, \qquad (11)$$

it is evident that an increase in either of the ratios

$$\frac{c_{Fe^{+++}}}{c_{Fe^{++}}} \quad \text{or} \quad \frac{c_{Cu^{+}}}{c_{Cu^{++}}}$$

will make the observed e.m.f. more positive. Before considering methods by which E° may be determined let us investigate the connection between the platinum acting as a redox electrode and as a hydrogen electrode.

Relation Between Oxidation-reduction Potentials and Hydrogen Ion Concentration.—Previously in this book we have assumed that a platinum electrode immersed in an aqueous solution is a hydrogen electrode, *i.e.*, an electrode reversible to hydrogen ions. What is the connection between a hydrogen platinum electrode and a redox platinum electrode and how does the potential of the latter vary with the pH? The first question can be answered by considering the changes which occur in going

* In Eqs. (9) and (10) the constants $\mathbf{E}^\circ$ include the constant for the electron in the metal.

over from a hydrogen electrode in a one normal hydrochloric acid solution to a ferric-ferrous electrode. Let us assume that the ratio $c_{Fe^{+++}}/c_{Fe^{++}}$ is always maintained equal to one so that the logarithm of this quantity drops out of the equation for the e.m.f. Let us also maintain the pH at unity. When the ferric-ferrous solution is added to the hydrochloric acid, the following reaction takes place:

$$Fe^{+++} + \tfrac{1}{2}H_2 \rightarrow H^+ + Fe^{++}, \tag{12}$$

but if the pH and the ferric-ferrous ratio are maintained constant it is evident that the partial pressure of hydrogen gas will soon fall to a very low value. The e.m.f. of the half cell

$$H^+ \mid H_2,\ Pt \tag{B}$$

in which the reaction $H^+ + \epsilon^- \rightarrow \tfrac{1}{2}H_2$ takes place is given by the equation

$$E = \frac{RT}{F} \ln \frac{c_{H^+}\mathbf{f}_{H^+}}{P_{H_2}^{1/2}} \tag{13}$$

since $\mathbf{E}°$ for the hydrogen electrode is by definition set equal to unity. Equation (13) tells us that the e.m.f. of cell (B) becomes more positive the lower the pressure of the hydrogen gas. The potential of the half cell

$$1.0\ N\ HCl,\ Fe^{+++},\ Fe^{++} \mid Pt \tag{C}$$

is 0.7 v. referred to the normal hydrogen electrode. We might be inclined to consider this high positive voltage as being due to a decrease in the hydrogen gas pressure of cell (C) rather than due to the oxidation-reduction potential of the ferric-ferrous combination. However, the partial pressure of hydrogen gas which satisfies Eq. (13) is about 10^{-27} atm., a pressure which is produced by only one molecule in 37,000 l. It is quite impossible to conceive of a hydrogen electrode being in equilibrium with such a small partial pressure of hydrogen as this. From a thermodynamic standpoint it is immaterial which mechanism we accept, it is possible to prove mathematically that the two mechanisms are equivalent to each other. The mass action expression for Eq. (12) is (at equilibrium)

$$K = \frac{c_{H^+}\mathbf{f}_{H^+}c_{Fe^{++}}\mathbf{f}_{Fe^{++}}}{P_{H_2}^{1/2}c_{Fe^{+++}}\mathbf{f}_{Fe^{+++}}},$$

or

$$\frac{c_{H^+}\mathbf{f}_{H^+}}{P_{H_2}^{1/2}} = K\frac{c_{Fe^{+++}}\mathbf{f}_{Fe^{+++}}}{c_{Fe^{++}}\mathbf{f}_{Fe^{++}}}. \tag{14}$$

Substituting this value for $c_{H^+} . \mathbf{f}_{H^+}/P_{H_2}^{1/2}$ into Eq. (13) we obtain

$$E_C = \frac{RT}{F}\ln K + \frac{RT}{F}\ln\frac{c_{Fe^{+++}}\mathbf{f}_{Fe^{+++}}}{c_{Fe^{++}}\mathbf{f}_{Fe^{++}}} \tag{15a}$$

which is identical with Eq. (10) since the constant $(RT/F)\ln K$ is readily identified as the constant $\mathbf{E}°$. Thus, from the standpoint of thermodynamics it is immaterial whether we consider the ferric-ferrous electrode as a hydrogen electrode or as a redox electrode; both concepts lead to the same equation. However, on a molecular viewpoint the mechanism stipulating that the ferric-ferrous electrode acts as a hydrogen electrode seems to be physically impossible.

The question concerning the effect of change in hydrogen ion concentration upon the e.m.f. of a redox cell is easily answered by measuring the e.m.f. of the cell

$$\text{Pt, H}_2 \left| \begin{matrix} \text{HCl} \\ c_{H^+}\mathbf{f}_{H^+} = 1 \end{matrix} \right\| \text{salt bridge} \left\| \begin{matrix} c_{ox.} = c_{red.} \\ \text{pH} = x \end{matrix} \right| \text{Pt} \qquad (D)^*$$

The e.m.f. of the standard hydrogen electrode is zero; hence the e.m.f. of cell (D) is given by the equation

$$E_h = \mathbf{E}°' + \frac{RT}{nF}\ln\frac{c_{ox.}\mathbf{f}_{ox.}}{c_{red.}\mathbf{f}_{red.}}, \tag{16}$$

* To be perfectly precise the concentration of the hydrochloric acid in the standard hydrogen electrode should be such that $m\gamma$ equals unity rather than $c\mathbf{f}$. The relations between m and c, γ and $\mathbf{f}$ and $E°$ and $\mathbf{E}°$ are given by the equations

$$\log m = \log c - \log\left(1 + \frac{n_2 w_2}{n_1 w_1}\right) - \log d, \tag{15b}$$

where d is the density of the solution, n_1, n_2, w_1, w_2 the number of moles and molecular weights of solvent and solute, respectively,

$$\log \gamma = \log \mathbf{f} - \log\left\{1 + \frac{n_2 w_2}{n_1 w_1}\right\} \tag{15c}$$

$$E° = \mathbf{E}° - \left(\frac{\nu_+ + \nu_-}{\nu_+ z_+}\right)\frac{RT}{F}\ln d_{H_2O}. \tag{15d}$$

The difference between $E°$ and $\mathbf{E}°$ amounts to 0.00013, 0.0005, 0.0026 v. at 25, 50, and 100°, respectively. Hence at 25°, $E°$ may be assumed equal to $\mathbf{E}°$ and we introduce no practical error by substituting $c\mathbf{f}$ for $m\gamma$.

where E_h signifies the e.m.f. of any cell measured against the normal hydrogen electrode. But $c_{ox.}$ is equal to $c_{red.}$ in this particular instance, and if we assume that the activity coefficients are also equal, the measured e.m.f. E_h becomes equal to $E^{\circ\prime}$.* The hydrogen ion concentration of the redox half cell of (*D*) can be varied over a considerable range and the e.m.f. of the cell (*D*) measured. The observed e.m.f. according to Eq. (15*a*) should be independent of the pH, but in many cases this is not true. In Fig. 2† values of $E^{\circ\prime}$ for a number of redox systems are plotted as a function of the pH. Curve 1, representing the relation of the potential of the hydrogen electrode at one atmosphere pressure of hydrogen gas to the pH is a perfectly straight line and the most negative of all the curves. The highest curve, curve 6, is the theoretical potential of the oxygen electrode. This electrode has not been experimentally realized as yet. The ferric-ferrous electrode (curve 5) which can only be investigated in acid solutions gives a potential much nearer to the potential of the oxygen electrode than to that of the hydrogen electrode and apparently functions independently of the pH over the short range investigated. The ferri-ferrocyanide electrode (curve 4) is independent of the pH except in acid solutions while the quinhydrone electrode (curve 3) and the β-anthraquinone sulfonate β-anthrahydro-

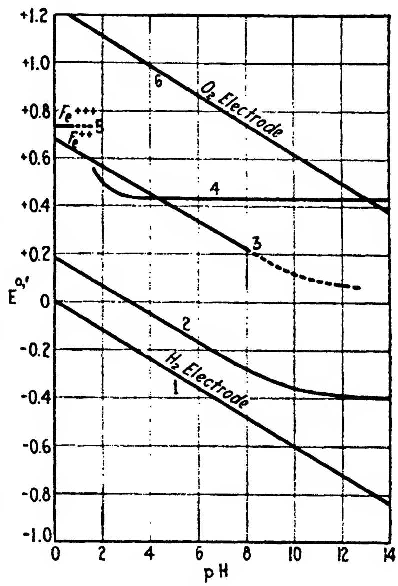


FIG. 2.

* The subscript *ox.* → *red.* which has been added to E° will henceforth be omitted since E° always refers to the electrode reaction oxidant → reductant.

† Fig. 2 is taken from W. M. Clark, "The Determination of Hydrogen Ions," p. 387, Williams & Wilkins Company, Baltimore, 1928. See also L. Michaelis, "Oxidation—Reduction Potentials," J. B. Lippincott Company, Philadelphia, 1930.

quinone sulfonate electrode (curve 2) (to be discussed later) give values directly proportional to the pH at pH values below 8 but not above. The oxidants of each of the electrodes become stronger as one goes up the graph, *i.e.*, oxygen is the most powerful oxidizing agent and hydrogen is the most powerful reducing agent. There are substances which are still stronger reducing agents than hydrogen, but they are unstable in aqueous solutions reducing the hydrogen ions in water to gaseous hydrogen.

The data plotted in Fig. 2 demonstrate that a change in pH has much less effect on the potential of an inorganic redox electrode than on an organic redox electrode, being due to the fact that, as explained below, the organic reductants are weak acids as well as reducing agents. Before describing the important studies made by Clark, Conant, Fieser, and others on the potentials of reversible and irreversible organic redox electrodes, let us first consider the determination of the standard electrode potentials of the inorganic oxidation-reduction systems.

Standard Oxidation-reduction Potentials.—By referring to Eq. (1) it is evident that the observed e.m.f. of an oxidation-reduction electrode when measured against the normal hydrogen electrode becomes equal to the standard redox potential, E°, when $m_{ox.} = m_{red.}$, *provided the solution is an ideal solution.* Since the behavior of a solution is ideal only at zero concentration, we must measure E_h over a range of concentrations of the oxidizing and reducing constituents, and extrapolate the observed values of E_h to zero concentration in order to obtain $E^{\circ\prime}$. But the $E^{\circ\prime}$ values are a function of the hydrogen ion concentration; hence these values must be extrapolated to zero concentration of hydrogen ion to get the true value of E°. Thus Popoff and Kunz* have determined the standard electrode potential of the ferric-ferrous electrode in a manner closely similar to this procedure. Some typical data for E_h over a range of total iron concentrations (always, however, with the ratio $m_{Fe^{+++}}/m_{Fe^{++}}$ equal to unity) are given in Table I.

By extrapolating values of E_h to zero iron concentration values of $E^{\circ\prime}$ are obtained (Table II). The data of Table II demonstrate that the standard electrode potential of the ferric-ferrous electrode definitely varies with change of pH. According to the

* S. Popoff and A. H. Kunz, *J. Am. Chem. Soc.*, **51**, 382 (1929).

data plotted in Fig. 2, $E^{\circ\prime}$ for the ferric-ferrous electrode is independent of the pH; there is a slight discrepancy here therefore.

TABLE I.—E_h VALUES OF THE FERRIC-FERROUS ELECTRODE AT 25°C.
(*Data of Popoff and Kunz*)
$m_{Fe^{+++}} = m_{Fe^{++}}$

0.05m HCl		0.5m HCl		1m HCl	
Total iron, moles per 1,000 g. of soln.	E_h	Total iron	E_h	Total iron	E_h
0.0733	0.72449	0.0720	0.70359	0.0569	0.69642
0.0376	0.72759	0.0363	0.70634	0.0290	0.69801
0.0191	0.73137	0.0183	0.70817	0.0124	0.69891
0.00943	0.73372	0.00925	0.70902	0.00609	0.69931
0.00532	0.73597	0.00453	0.70937	0.00348	0.69967
0.00255	0.73719	0.00248	0.70957		

TABLE II.—$E^{\circ\prime}$ VALUES OF THE FERRIC-FERROUS ELECTRODE AT 25°C.
(*Data of Popoff and Kunz*)

Acid concentration........	0.05	0.1	0.2	0.5	1.0
$E^{\circ\prime}$......................	0.7386	0.7311	0.7222	0.7098	0.7000

Popoff and Kunz finally determine E° by plotting the data of Table II against the hydrochloric acid concentration. On extrapolation to zero hydrochloric acid concentration, the value 0.7477 for E° results.

"The "International Critical Tables"* gives values of E° for many other redox electrodes, some of which are listed in Table III. The sign of the electrode is the sign of the cell

$$\mathrm{Pt, H_2} \left| \begin{matrix} \mathrm{H^+} \\ m_{\mathrm{H^+}}\gamma_{\mathrm{H^+}} = 1 \end{matrix} \right\| \; m_{red.} = m_{ox.} \left| \mathrm{Pt.} \right.$$

In writing down a cell for the determination of standard electrode potentials, the normal hydrogen electrode is always written at the left.

In Table III the most powerful oxidizing agents are at the top, the most powerful reducing agents at the bottom. From the table we can learn at a glance which ions will oxidize or reduce

* Vol. VI, p. 332; see also GERKE, *Chem. Rev.*, **1**, 377 (1925).

other ions at molal concentrations. The use of this table may be briefly demonstrated by a few examples. The e.m.f. of the ferric-ferrous and cuprous-cupric cell (*A*) may be readily cal-

TABLE III.—STANDARD OXIDATION AND REDUCTION ELECTRODE POTENTIALS

Electrode	Electrode reaction	$E°$ at 25°C.
Co^{+++}, Co^{++}, Pt	$Co^{+++} + \epsilon^- = Co^{++}$	1.817
Ce^{++++}, Ce^{+++}, Pt	$Ce^{++++} + \epsilon^- = Ce^{+++}$	1.55
Sn^{++++}, Sn^{++}, Hg	$Sn^{++++} + 2\epsilon^- = Sn^{++}$	1.256
Fe^{+++}, Fe^{++}, Pt	$Fe^{+++} + \epsilon^- = Fe^{++}$	0.7477
$\frac{1}{2}I_2$, I^-, Pt	$\frac{1}{2}I_2 + \epsilon^- = I^-$	0.5345
H_3AsO_4, H_3AsO_3, H^+, Pt	$H_3AsO_4 + 2H^+ + 2\epsilon^- = H_3AsO_3 + H_2O$	0.57
$K_3Fe(CN)_6$, $K_4Fe(CN)_6$, Pt	$K_3Fe(CN)_6 + K^+ + \epsilon^- = K_4Fe(CN)_6$	0.4866
$CuCl_2$, CuCl, Pt	$Cu^{++} + 2Cl^- + \epsilon^- = CuCl_2^-$	0.455
Ti^{+++}, Ti^{++}, Hg	$Ti^{+++} + \epsilon^- = Ti^{++}$	0.37
$Ti(SO_4)_2$, $SO_4^=$, Ti^{+++}, Pt	$Ti(SO_4)_2 + \epsilon^- = Ti^{+++} + 2SO_4^=$	0.04
Cr^{+++}, Cr^{++}, Hg	$Cr^{+++} + \epsilon^- = Cr^{++}$	−0.40

culated for unit values of the ratio $m_{ox.}/m_{red.}$ (in an ideal solution) by merely subtracting 0.455 from 0.7477. The equilibrium constant of the typical reaction

$$Fe^{+++} + I^- \rightleftarrows \tfrac{1}{2}I_2 + Fe^{++}$$

may be computed from the equation

$$RT \ln K = F(E^\circ_{Fe^{+++} \to Fe^{++}} - E^\circ_{\frac{1}{2}I_2 \to I^-}) = 0.2132F$$

since

$$E^\circ = \frac{RT}{nF} \ln K$$

(see Chap. XVI). Hence

$$K = \frac{m_{I_2}^{1/2} \cdot m_{Fe^{++}}}{m_{Fe^{+++}} \cdot m_{I^-}} = 3.6 \times 10^3.$$

If the ratio Fe^{+++}/Fe^{++} is maintained equal to unity, the reaction will proceed until the concentration of the iodine is roughly ten million times as great as that of the iodide ion; in other words, the iodide ion will be practically completely oxidized. Such calculations are very useful in qualitative and quantitative analysis.

Activity Coefficients of Oxidizing and Reducing Ions.—The validity of Eq. (1) depends upon the relative values of the activity coefficients of the oxidant and reductant, respectively. If $f_{ox.}$ equals $f_{red.}$, the activity coefficients will cancel each other, and the ideal Eq. (1) is obtained. But since the oxidant and reductant must differ in charge from each other by at least one unit, we can predict from the theory of Debye and Hückel that in general $f_{ox.}$ will never equal $f_{red.}$ except at zero concentration. The equation for the activity coefficient of an ion as given by the Debye and Hückel theory is [Eq. (XVIII-42)],

$$\ln f_i = -z_i^2 k\sqrt{c}$$

where k is a constant for a given temperature and solvent. In the case of the ferric and ferrous ions, the ratio $\ln (f_{+++}/f_{++})$ is equal to

$$-(z_{+++}^2 - z_{++}^2)k\sqrt{c}.$$

The variation of the logarithm of the activity coefficient ratio from zero [in an ideal solution $\ln (f_{+++}/f_{++})$ would be zero] is proportional, therefore, to the difference between the squares of the valences of the oxidant and reductant, respectively. Since $z_{ox.}$ never equals $z_{red.}$, it follows that $f_{ox.}$ will never equal $f_{red.}$ except at zero concentration.

No comprehensive investigation of the activity coefficients of oxidizing and reducing ions has ever been undertaken.*

Oxidation-reduction Potentials in Reversible Organic Systems.—An important development of electrochemistry in the field of organic chemistry which began about 1920 consists in the measurement and interpretation of oxidation and reduction potentials of both reversible and irreversible organic reactions.† Many reversible organic systems have been studied:‡ as an

* The above discussion relating the activity coefficients of the oxidizing and reducing ions to the Debye theory is due to Glasstone, "The Electrochemistry of Solutions," Methuen & Co. Ltd., London, 1930.

† See the review by W. M. Clark, *Chem. Rev.*, **2**, 127 (1925)—reversible systems—and by J. B. Conant, *ibid.*, **3**, 1 (1926)—irreversible systems.

‡ Some recent papers have been published by the following: W. M. Clark and Marie E. Perkins, *J. Am. Chem. Soc.*, **54**, 1228 (1932); L. F. Fieser and E. M. Dietz, *ibid.*, **53**, 1128 (1931); J. B. Conant and C. O. Tongberg, *J. Biol. Chem.*, **86**, 733 (1930). Considerable data concerning e.m.f. cells involving the oxidation and reduction of organic compounds are given by

example of these let us consider the system anthraquinone-2, 7-disulfonic acid and its reductant.* Anthraquinone-2, 7-disulfonic acid may be readily reduced in aqueous solution by reducing agents such as sodium hydrosulfite and titanous chloride. By carrying out a potentiometric titration (potentiometric titrations are described in the next chapter) it is possible to follow the course of the reduction to determine the point of complete reduction. When the amount of reducing agent necessary for complete reduction is known, it is an easy matter to calculate from the e.m.f. data the electrode potential corresponding to the half reduction point. Since $c_{red.} = c_{ox.}$ at the half reduction point $E^{\circ,\prime}$ is readily determined, *i.e.*, at the half reduction point, the observed e.m.f. is equal to $E^{\circ,\prime}$ (assuming ideal solutions).† A typical titration curve for anthraquinone-2, 7-disulfonic acid at a pH equal to 3.44 is shown in Fig. 3 where abscissas are the percentage of reduction and ordinates the observed, E_h, e.m.f. values. At the 50 per cent reduction point, $E^{\circ,\prime}$ is read off the graph to be 0.031 v.

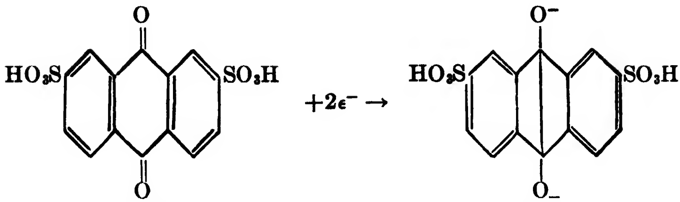
Values of $E^{\circ,\prime}$ so determined vary considerably with the pH, Fig. 4.

This interesting behavior, which is typical of a large number of organic oxidation and reduction systems, can be understood on the assumption that the hydroxyl hydrogens of the hydroquinone are weakly acidic. The sulfonic hydrogens are almost completely ionized and need not be considered further here. When the electric current flows through the redox cell in such a direction that the anthraquinone is reduced, the following reaction takes place at the platinum electrode:

Conant, "International Critical Tables," Vol. VI, p. 333, McGraw-Hill Book Company, Inc., New York, 1929.

* J. B. Conant, H. M. Kahn, L. F. Fieser, and S. S. Kurtz, Jr., *J. Am. Chem. Soc.*, **44**, 1382 (1922).

† Another indirect method of determining oxidation-reduction potentials consists in the use of "potential mediators" so-called. A small amount of an inorganic oxidizing or reducing agent is added to a sluggish system; the inorganic agent reacts rapidly with the sluggish redox system until it attains the same potential. A platinum electrode immersed in the solution will measure the potential of the inorganic system and thus indirectly the potential of the sluggish system. Loimaranta, [*Z. Elektrochem.*, **13**, 33, (1907)], used potassium iodide as a potential mediator in studying the oxidation-reduction potential of acid arsenate-arsenite mixtures.



Anthraquinone-2, 7-disulfonic acid

Anthrahydroquinone-2, 7-disulfonic acid ion

In order to simplify the writing of equations let us represent the oxidized anthraquinone by Ao and the reduced un-ionized anthra-

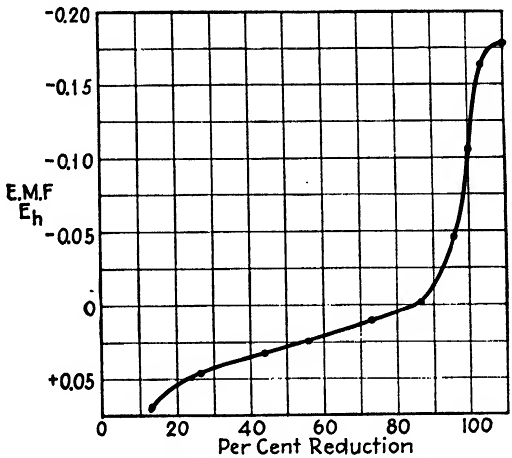


FIG. 3.—A typical redox titration curve.

hydroquinone by ArH_2. The above electrode reaction can then be written

$$Ao + 2\epsilon^- \rightleftarrows Ar^= . \tag{17}$$

The equation for the e.m.f. of the anthraquinone electrode is

$$E_h = \mathbf{E}^\circ - \frac{RT}{2F} \ln \frac{c_{Ar^=}}{c_{Ao}}, \tag{18}$$

provided we assume that the electrode reaction concerns only Ao and the anion $Ar^=$ and not the ion ArH^- or the undissociated molecule ArH_2. As the anthraquinone is reduced to the anthrahydroquinone, the following equilibria are set up:

$$ArH_2 \rightleftarrows ArH^- + H^+ \tag{19a}$$

$$ArH^- \rightleftarrows Ar^= + H^+, \tag{19b}$$

for which we can write the equilibrium constant equations (activity coefficients are necessarily omitted):

$$K_1 = \frac{c_{\mathrm{ArH^-}} \cdot c_{\mathrm{H^+}}}{c_{\mathrm{ArH_2}}} \tag{20a}$$

and

$$K_2 = \frac{c_{\mathrm{Ar^{--}}} \cdot c_{\mathrm{H^+}}}{c_{\mathrm{ArH^-}}}. \tag{20b}$$

In carrying out the oxidation-reduction titration illustrated in Fig. 3, the concentration of reductant measured is the total concentration of all the reductant species, *i.e.*,

$$c_{red.} = c_{\mathrm{Ar^{--}}} + c_{\mathrm{ArH^-}} + c_{\mathrm{ArH_2}}. \tag{21}$$

Similarly the value of $E^{\circ\prime}$ is the value of E_h when $c_{red.} = c_{\mathrm{Ao}}$ and not when $c_{\mathrm{Ar^{--}}} = c_{\mathrm{Ao}}$.

Eliminating $c_{\mathrm{Ar^{--}}}$, $c_{\mathrm{ArH^-}}$ and $c_{\mathrm{ArH_2}}$, quantities which are unknown from Eqs. (18), (20), and (21), the desired equation is obtained,

$$E_h = \mathbf{E}^\circ - \frac{RT}{2F} \ln \frac{c_{red.}}{c_{\mathrm{Ao}}} + \frac{RT}{2F} \ln \left[K_1K_2 + K_1c_{\mathrm{H^+}} + c^2_{\mathrm{H^+}}\right] - \frac{RT}{2F} \ln K_1K_2. \tag{22}$$

By setting $c_{red.} = c_{\mathrm{Ao}}$, which is what we do when we calculate $E^{\circ\prime}$, Eq. (22) becomes

$$E^{\circ\prime} = \mathbf{E}^\circ + \frac{RT}{2F} \ln \left[K_1K_2 + K_1c_{\mathrm{H^+}} + c^2_{\mathrm{H^+}}\right] - \frac{RT}{2F} \ln K_1K_2. \tag{23}$$

Thus it appears that according to the above theory, $E^{\circ\prime}$ should not be a constant, but should really be a function of the pH. It is possible to distinguish three different situations; first if $c^2_{\mathrm{H^+}} > K_1c_{\mathrm{H^+}} > K_1K_2$ Eq. (23) can be written

$$\begin{aligned} E^{\circ\prime} &= \mathbf{E}^\circ + \frac{RT}{F} \ln c_{\mathrm{H^+}} - \frac{RT}{2F} \ln K_1K_2 \\ &= k' + \frac{RT}{F} \ln c_{\mathrm{H^+}} \end{aligned} \tag{24}$$

which is the usual equation for the hydrogen electrode. At low values of the pH, the hydrogen ion concentration will be large and the $E^{\circ\prime}$ values should be given by Eq. (24). A reference to Fig. 4 demonstrates that the theory is accurately and quantitatively verified in this respect, the slope $dE^{\circ\prime}/d\mathrm{pH}$ has the correct value, -0.059.

Second, if the pH is increased, $c^2_{H^+}$ will become smaller than $K_1c_{H^+}$ and over a limited pH range, we may expect Eq. (23) to reduce to

$$E^{\circ\prime} = \mathbf{E}^\circ + \frac{RT}{2F} \ln K_1c_{H^+} - \frac{RT}{2F} \ln K_1K_2 = k'' + \frac{RT}{2F} \ln c_{H^+}. \quad (25)$$

According to Eq. (25) $E^{\circ\prime}$ values should still be a function of the hydrogen ion concentration, but the slope $dE^{\circ\prime}/d\text{pH}$ should

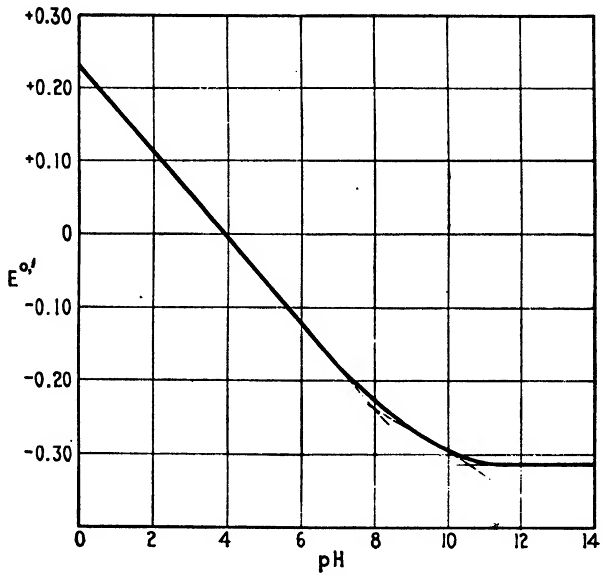


FIG. 4.—$E^{\circ\prime}$ values for anthraquinone -2, 7-disulfonic acid and its reductant.

be only half as great as the slope of Eq. (24). The data of Fig. 4 agree with this prediction.

Third, if the hydrogen ion concentration is reduced to such a low value that $K_1c_{H^+} < K_1K_2$, Eq. (23) becomes

$$E^{\circ\prime} = \mathbf{E}^\circ + \frac{RT}{2F} \ln K_1K_2 - \frac{RT}{2F} \ln K_1K_2 = \mathbf{E}^\circ \quad (26)$$

and the $E^{\circ\prime}$ values should be independent of the pH. This prediction is also verified by the data of Fig. 4.

It is easy to calculate values of K_1 and K_2 by finding the hydrogen ion concentration at the intersections of the extrapolated straight lines of Fig. 4.

By the methods illustrated above it is possible to obtain important information concerning many organic oxidizing and reducing agents; not only is it possible to determine their relative oxidizing power, but it is possible to calculate dissociation constants for the weak acids involved. Considerable information concerning the structure of these rather specialized compounds can also be inferred from the electrochemical measurements. In this connection the work of Conant, Fieser, and others* on the oxidation-reduction potentials observed in irreversible and unstable systems and systems capable of only a transitory existence is interesting and important. The data provide a more or less quantitative measure of the ease of oxidation in irreversible oxidation processes, but as the results are used chiefly in elucidating recondite questions of organic chemistry, they will not be described here.

Exercises

1. Calculate the mass action constant of the reaction

$$Ce^{++++} + Fe^{++} \rightleftarrows Fe^{+++} + Ce^{+++}.$$

2. Estimate K_1 and K_2 for anthrahydroquinone-2, 7-disulfonic acid.

* J. B. Conant, *Chem. Rev.*, **3**, 1 (1926); J. B. Conant, J. G. Aston, and C. O. Tongberg, *J. Am. Chem. Soc.*, **52**, 407 (1930); L. F. Fieser, *ibid.*, **52**, 4915, 5204 (1930); E. G. Ball and W. M. Clark, *Proc. Nat. Acad. Sci.*, **17**, 347 (1931).

CHAPTER XXIV

POTENTIOMETRIC METHODS OF ANALYSIS

By measuring the change of e.m.f. at a single electrode as the concentration of the electrolyte in which the electrode is immersed is changed, it is possible to obtain some idea concerning the concentration or change in concentration of a single ionic constituent of the solution. The impossibility, however, of completely eliminating the liquid-junction potential and the concomitant lack of knowledge concerning the ionic activity coefficient prevent exact measurements of ionic concentrations in solution by the measurement of the e.m.f. of cells with liquid junctions. Nevertheless, potentiometric methods of analysis are exceedingly useful and find widespread application since in many analytical titrations it is not necessary to know exact values of ionic concentration. Important exceptions to this statement are the potentiometric experiments determining the hydrogen ion concentration, or pH, of solutions, experiments in which we attempt to determine the hydrogen ion concentration exactly. We do not do so due to the liquid-junction potential and activity coefficient difficulties mentioned in the foregoing, yet these experiments yield results of great significance since the pH numbers so obtained have been calibrated in terms of observable phenomena. As a matter of convenience we shall continue to speak of the potentiometric measurement of ionic concentration with the understanding that these measurements are subject to the inherent limitation of the liquid-junction uncertainty.

The Determination of the pH.—The influence of the hydrogen ion concentration upon all kinds of industrial, inorganic, biological, and physiological processes has given to the measurement of hydrogen ion concentration, or rather pH, a great practical significance. The most accurate method of pH determination, the method which gives standard pH values to which all other values are referred, is based on the use of the hydrogen electrode. An inert electrode such as an electrode of platinum,

palladium or gold when coated with platinum or palladium black and immersed in a solution develops a potential on its surface which is a function of the concentration and activity coefficient of the hydrogen ions in the solution and of the partial pressure of the gaseous hydrogen. This is a "hydrogen electrode," but it must always be used in conjunction with some reference electrode such as the calomel half cell (Chap. XIV, Fig. 8).

There have been countless cells designed which bring together a hydrogen electrode and the reference half cell.* The principles which must be borne in mind in the design of a hydrogen electrode vessel are: first, the vessel must be of a convenient size, *i.e.*, if only a small body of solution is available, the vessel must be made small; second, it must be possible to make the liquid junction between the unknown solution and the reference electrode within the bore of a tube so that cylindrical symmetry is present, and it must be possible to renew the junction when necessary to rinse out the connecting tubes; third, the hydrogen gas must be as pure as possible and, for rapid measurements, it should be permitted to come into contact with the platinum through a thin film of liquid; fourth, it must be possible either to measure the temperature or to control the temperature of the cell; fifth, it is advisable to shake or rock the cell in order to attain equilibrium more quickly. All these principles were observed by Clark† in designing the hydrogen electrode vessel known as the "Clark rocking cell." The Clark rocking cell is illustrated in Fig. 1 where *M* refers to the standard saturated potassium chloride calomel electrode which is used in all the measurements. Since the potential of this saturated type of calomel electrode may not always have the same value, Clark introduced the accurately made tenth normal calomel electrodes *P* in order to standardize the saturated electrode *M*. The standardization is easily accomplished by opening *K* and filling *O* with saturated potassium chloride solution from the reservoir *N*.

The hydrogen cell *E* which is rocked by the eccentric *I* is connected to *M* by means of rubber tubing at *J*. The hydrogen

* The reader will find in the excellent monograph of William M. Clark, "The Determination of Hydrogen Ions," 3d ed., Williams & Wilkins Company, Baltimore, 1928, a wealth of experimental details covering all phases of pH measurements.

† W. M. Clark, *J. Biol. Chem.*, **23**, 475 (1915).

electrode is inserted at F, while the unknown solution in the reservoir D flows into E when the stopcock C is turned to the proper position. Solution or hydrogen gas may be drained off at B'. The procedure is to fill the vessel with water or solution and then to displace all the water with hydrogen. Solution is then admitted until the cell is half full. During the filling of the cell with solution, cock G is open and the cell is tipped back until the cock C is as low as possible. After closing cock G, cock C

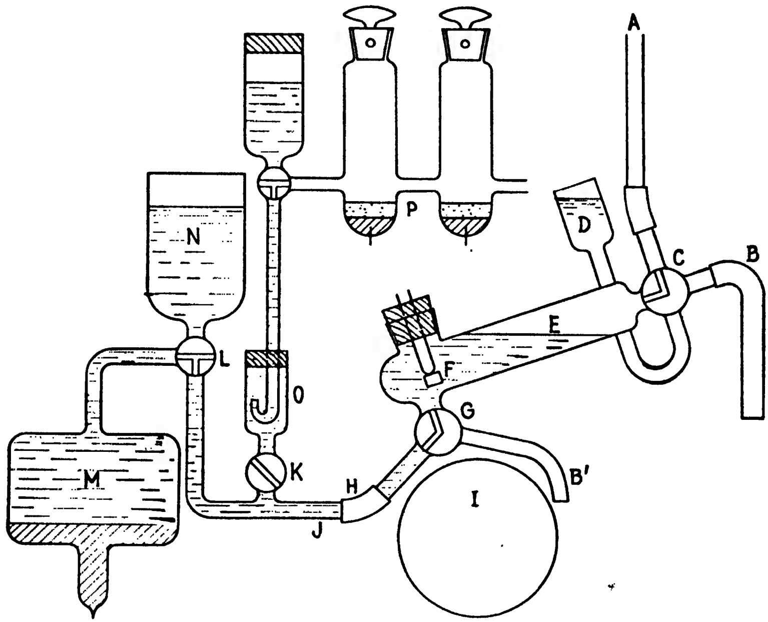


FIG. 1.—The Clark hydrogen electrode cell.

is opened so that the hydrogen gas by entering through A may exert a constant pressure on the liquid during the rocking. The rocking should be so adjusted that the electrode is alternately completely immersed and completely exposed to the hydrogen gas, and should be continued until the measured e.m.f. becomes constant. Before the e.m.f. can be measured, the rocking must be stopped so that the hydrogen electrode is immersed, and a liquid junction must be made at H. This is done by opening G, so that the potassium chloride solution may escape through B', at the same time pinching the rubber tube between J and H.

On turning G to the position in Fig. 1 and releasing the pinch, the unknown solution will flow into H making a broad junction with the salt-bridge solution inside the tube at H.

The Clark rocking cell is a particularly good cell because it allows the hydrogen gas to come into frequent contact with the electrode. Any oxygen that is in the hydrogen gas is removed by reduction on the surface of the platinum black. No new hydrogen gas is admitted; hence the hydrogen is gradually purified. In some hydrogen electrode vessels, hydrogen gas is bubbled continually over the electrode and if there is a slight trace of oxygen in the hydrogen, the potential at the electrode surface will be different from its true hydrogen electrode value. The Clark rocking cell overcomes this difficulty.

Having obtained a constant and reproducible value for the e.m.f. developed between the unknown solution and the standard calomel half cell, the question arises, how is the pH calculated from the observed data? Fundamentally, the calculations reduce to the calculation of the pH from e.m.f. values of the cell

$$\mathrm{Pt, H_2} \mid \mathrm{H^+}(m_{\mathrm{H^+}} \cdot \gamma_{\mathrm{H^+}} = x) \parallel \mathrm{H^+}(m_{\mathrm{H^+}} \cdot \gamma_{\mathrm{H^+}} = 1) \mid \mathrm{H_2, Pt} \qquad (A)$$

whose e.m.f. on neglecting the liquid junction is given by the equation [compare Eq. (XVI-11)],

$$E_A = E_{dil.} - E_{concn.} = \frac{RT}{F} \ln \frac{1}{m_{\mathrm{H^+}} \cdot \gamma_{\mathrm{H^+}}} \qquad (1)$$

or

$$E_A = 0.05912 \text{ pH} \qquad (2)$$

at 25°C. since the pH is defined by the equation

$$\mathrm{pH} = \log \frac{1}{m_{\mathrm{H^+}} \cdot \gamma_{\mathrm{H^+}}}. \qquad (3)$$

Actually we make measurements of the cell

$$\mathrm{Pt, H_2} \mid \mathrm{H^+}(m_{\mathrm{H^+}} \cdot \gamma_{\mathrm{H^+}} = x) \parallel \text{sat. KCl} \mid \mathrm{Hg_2Cl_2} \mid \mathrm{Hg}. \qquad (B)$$

If we know the e.m.f. of the cell (C),

$$\mathrm{Hg} \mid \mathrm{Hg_2Cl_2} \mid \text{sat. KCl} \parallel \mathrm{H^+}(m_{\mathrm{H^+}} \cdot \gamma_{\mathrm{H^+}} = 1) \mid \mathrm{H_2, Pt}, \qquad (C)$$

we can easily obtain the desired e.m.f., E_A, by adding the e.m.f. of (C) to the e.m.f. of B; that is

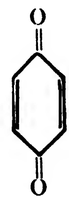
$$E_A = E_B + E_C. \qquad (4)$$

The value of cell (C) is the standard electrode potential of the saturated calomel electrode with opposite sign and is obtained by an extrapolation method. Clark* gives the value of cell (C) at 25°C. as -0.2458 v. The pH is calculated at 25°C., therefore, by the equation

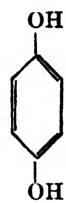
$$\text{pH} = \frac{E_B - 0.2458}{0.05912.} \tag{5}$$

The constants of Eq. (5) depend on the temperature; furthermore values of E_B must be corrected to unit partial pressure of the gaseous hydrogen if the hydrogen gas pressure is not at one atmosphere during the e.m.f. measurement.

The Quinhydrone Electrode.—Another electrode that is used extensively in pH measurements is the quinhydrone electrode, an electrode which consists of a bright platinum electrode immersed in a saturated solution of quinhydrone. Quinhydrone is an equimolecular compound of quinone



and of hydroquinone



Since the solution is always saturated with the quinhydrone, the following equilibria can be written

$$\underset{\text{solid}}{Q.H_2Q} \rightleftarrows \underset{\text{solution}}{Q.H_2Q} \rightleftarrows \underset{\text{solution}}{Q + H_2Q,} \tag{5}$$

where $Q.H_2Q$ represents quinhydrone, Q quinone and H_2Q, hydroquinone. The hydroquinone can also enter into the equilibria

* W. M. Clark, "The Determination of Hydrogen Ions," p. 672.

$$H_2Q \rightleftarrows HQ^- + H^+ \tag{6a}$$
$$HQ^- \rightleftarrows Q^= + H^+. \tag{6b}$$

The e.m.f. of the quinhydrone electrode is given by the equation

$$E_h = E^\circ + \frac{RT}{2F} \ln \frac{m_Q \cdot \gamma_Q}{m_{Q^=} \cdot \gamma_{Q^=}} \tag{7}$$

since the quinhydrone electrode is essentially an oxidation-reduction electrode. From equilibrium (6b) we have the thermodynamic L.M.A. equation

$$m_{Q^=} \cdot \gamma_{Q^=} = \frac{K_2 \cdot m_{HQ^-} \cdot \gamma_{HQ^-}}{m_{H^+} \cdot \gamma_{H^+}}, \tag{8a}$$

and from equilibrium (6a), the thermodynamic L.M.A. equation

$$m_{HQ^-} \cdot \gamma_{HQ^-} = K_1 \cdot \frac{m_{H_2Q} \cdot \gamma_{H_2Q}}{m_{H^+}\gamma_{H^+}}. \tag{8b}$$

Eliminating $m_{HQ^-} \cdot \gamma_{HQ^-}$ from Eqs. (8a) and (8b)

$$m_{Q^=} \cdot \gamma_{Q^=} = \frac{K_1 \cdot K_2 \cdot m_{H_2Q} \cdot \gamma_{H_2Q}}{(m_{H^+} \cdot \gamma_{H^+})^2}, \tag{9}$$

which on introduction into Eq. (7) yields the equation

$$E_h = E^\circ + \frac{RT}{2F} \ln \frac{m_Q \cdot \gamma_Q}{m_{H_2Q} \cdot \gamma_{H_2Q}} - \frac{RT}{2F} \ln K_1K_2 + \frac{RT}{F} \ln m_{H^+} \cdot \gamma_{H^+}. \tag{10}$$

In acid solutions the ionization of the hydroquinone will be nearly completely repressed (because K_1 and K_2 are very small) so that the concentration of the quinone and undissociated hydroquinone may be set equal to each other. Under these conditions the second term of the right-hand side of Eq. (10) drops out and the equation for the potential of the quinhydrone electrode becomes

$$E^{\circ,\prime} = k + \frac{RT}{F} \ln m_{H^+} \cdot \gamma_{H^+}, \tag{11}$$

which is the correct equation for the hydrogen electrode. Thus we see that the quinhydrone electrode will act as a true hydrogen electrode providing the solution is not too basic. As a matter of fact the quinhydrone electrode gives accurate pH values up to a pH of 8. Morgan and Lammert* have recently carried out an

* Morgan, Lammert, and Campbell, *J. Am. Chem. Soc.*, **53**, 454, 597 (1931); Morgan and Lammert, *ibid.*, **53**, 2154 (1931); Lammert and

extensive investigation of the properties of the quinhydrone electrode and they conclude that "while the quinhydrone half cell makes an excellent secondary standard since it gives extremely precise results when the conditions can be made optimum, it must be used with great discretion as a working electrode, its use being preceded by a study of its reproducibility in the system under investigation."

In making a pH measurement the solution is saturated with quinhydrone and the potential of the platinum electrode measured against some reference electrode such as the saturated calomel electrode. The constant k of Eq. (11) is equal to 0.6990 v. at 25°C.* Other electrodes used in pH measurements are the glass electrode (see next chapter), and the antimony-antimony oxide electrode and other metal oxide electrodes. These metal-metallic oxide electrodes must be calibrated before use.

Direct Potentiometric Titrations.—The pH measurements described above consist in the determination of the concentrations of the hydrogen ion which exist at the moment of observation but do not give any information concerning the total amount of hydrogen ion in the solution or the amount of hydrogen ion which might arise from further ionization of un-ionized acids. In order to calculate total quantities of hydrogen ion, or of acids or bases or of other substances it is obviously necessary to carry out titrations. Potentiometric titrations are of two general types: direct and differential. Both of these types of titrations have been applied in the analysis of acids and bases (acidimetry), in the analysis of chlorides and other substances which form insoluble compounds during the titration (precipitimetry) and in the analysis of oxidizing or reducing agents (oxidimetry). Direct titration data may also be used to calculate dissociation constants while activity coefficients may be estimated from the data of differential titrations in certain cases.

MORGAN, *ibid.*, **54**, 910 (1932); See also HARNED and WRIGHT, *ibid.*, **55**, 4849 (1933); HOVORKA and DEARING, *ibid.*, **56**, 243 (1934).

* H. T. S. Britton, "Hydrogen Ions," D. Van Nostrand Company, Inc., New York, 1929, gives the following equation for k between 0° and 37°C.:

$$k = 0.7175 - 0.00074t,$$

where t is the temperature in degrees centigrade.

An abrupt change in the concentration of an ion will cause an abrupt change in the potential of an electrode reversible to the ion in question. In the course of an acid-base titration there is a sudden and manyfold change in the hydrogen ion concentration in the neighborhood of the end point, a change which causes a rapid change in the potential of the electrode. This definite increase or decrease in the measured e.m.f. serves as an excellent indicator for the titration end point, and makes possible both the direct and differential titrations.

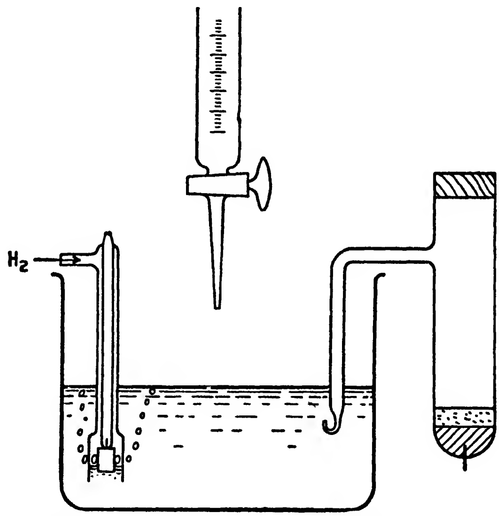


FIG. 2.—Potentiometric acid-base titration cell.

The electrode vessel necessary for a direct potentiometric titration may be the simplest possible type or it may be rather complicated. A beaker may serve as the vessel. In this case the end of the potassium chloride salt bridge is dipped into the solution in the beaker in order to make connection with the calomel electrode, and the beaker is placed under the tip of a burette. A hydrogen electrode is also dipped into the solution, as represented in Fig. 2. The titration is carried out in exactly the same manner as a colorimetric titration with the exception that the e.m.f. of the cell is read instead of the color of the solution examined. If the acid to be titrated with standard base has an original concentration of one normal, the initial e.m.f. is about

0.2 v. with the calomel electrode positive. As base is added, the hydrogen ion concentration of the solution diminishes and the e.m.f. rises until at the end point there is a sudden increase in the e.m.f.; the increase being greater the stronger the acid. If more base is added, the e.m.f. will continue to rise until it attains a value of over 1 v. At this point the solution will be approximately 0.1 *N* sodium hydroxide. However, in an ordinary titration only a sufficient number of e.m.f. values are determined

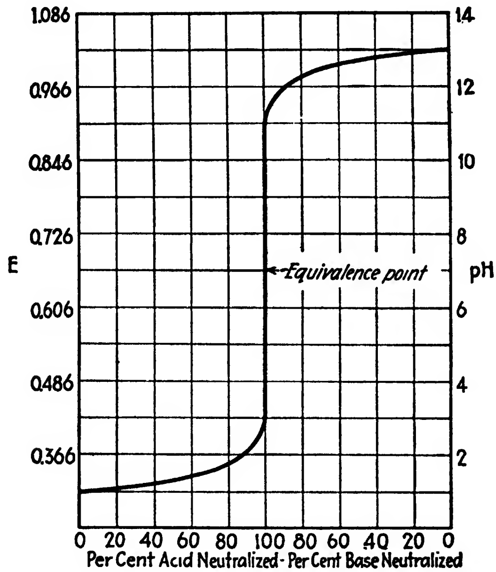


FIG. 3.—Theoretical titration curve of 0.1 *N* strong acid and strong base assuming constant volume.

beyond the end point to enable the end point to be found with precision. To estimate the end point accurately, the e.m.f. measurements may be plotted and the middle point of the inflection of the curve determined graphically. The course of a typical titration is illustrated in Fig. 3 where the observed e.m.f. is plotted as a function of the volume of standard base added.*

The titration apparatus becomes more complicated if the potassium chloride of the salt bridge can react with any ions in the solution. In investigating the possibilities of the accurate

* A general reference is: KOLTHOFF and FURMAN, "Potentiometric Titrations," John Wiley & Sons, Inc., New York, 1926.

potentiometric analysis of silver nitrate solutions, Lange and Schwartz* employed a chloride free ammonium nitrate bridge solution between the calomel electrode and the titration solution. They found it necessary to flow the ammonium nitrate solution slowly out of a side tube between the calomel electrode and the titration beaker so that chloride ions would not diffuse through the bridge solution into the silver nitrate solution. In the analysis of a solution for its silver ion content, a silver electrode must be used. Lange and Schwartz found it necessary to tap their silver electrode with an electric stirrer in order to dislodge any silver chloride that adhered to the silver electrode. The electric stirrer was also used to stir up the precipitated silver chloride that settled out on the bottom of the beaker. This was an essential precaution.

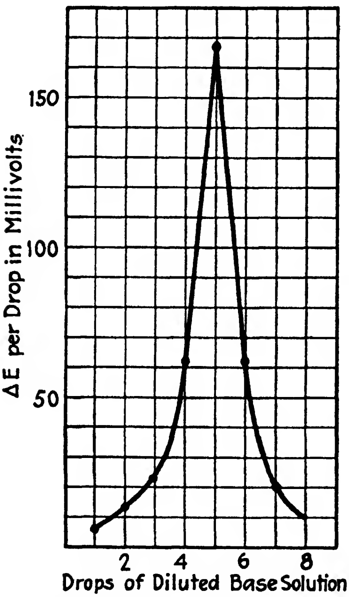


FIG. 4.—Titration of hydrochloric acid.

Oxidation-reduction titrations are carried out in the same manner as the acid-base titrations with the exception that it is usually inadvisable to titrate in the presence of oxygen of the air.

Titration of Monobasic Acids. The end point of an acid-base titration or as it is sometimes called the equivalence point (equivalent amounts of acid and base added) of the titration is indicated by the inflection point of the bilogarithmic e.m.f.-reagent volume curve as illustrated in Fig. 3. Since it is sometimes difficult to locate the exact point of inflection of a curve, it has become customary to plot the change of e.m.f. per single addition of base against the total amount of base added rather than the total e.m.f. of the cell. In this case the curve, Fig. 4, goes through a maximum at the equivalence point, enabling the end point of the titration to be found quite readily. To obtain

* LANGE and SCHWARTZ, *Z. Elektrochem.*, **32**, 240 (1926).

exact values of $\Delta E/\Delta V$ it is advisable that each increment of base ΔV be the same.

The change of e.m.f. at the equivalence point depends upon the strength of the acid and base used in the titration, the stronger the acid for any given base the greater will be the change of e.m.f. at the end point. Considering the titration of acids with a strong base, Roller* has calculated that no maximum in a titration curve will appear if $cK_A < 27K_W$. From a practical standpoint, however, an exact titration of a 0.1 N solution of an acid with $K_A = 10^{-9}$ is not possible. The effect of acid strength upon the height of the maximum is demonstrated by the data of Table I where $\Delta E/\Delta V$ is the change in e.m.f. per addition of 1.2×10^{-4} equivalent of base. The maximum in the case

TABLE I.—COMPARISON OF MAXIMA OBTAINED IN THE TITRATION OF A STRONG AND WEAK ACID

No. of base increments	$\Delta E/\Delta V$ Benzoic acid, $K = 6.5 \times 10^{-5}$	$\Delta E/\Delta V$ Hydrochloric acid
1	24	6,000
2	36	8,000
3	85	14,000
4	279	34,000
5	445	112,000
6	255	34,000
7	107	13,000

of hydrochloric acid is greater and sharper than it is in the case of benzoic acid.† The height of the maximum at the end point also depends on the volume of the solution at the end point, and on the number of equivalents of base added per single increment.

* P. S. ROLLER, *J. Am. Chem. Soc.*, **50**, 1 (1928). In this expression c is defined by the equation

$$\frac{1}{c} = \frac{1}{c_{acid}} + \frac{1}{c_{base}},$$

where c_{acid} and c_{base} are the initial concentrations of the weak acid and strong base, respectively.

† The data for hydrochloric acid were estimated from the paper of MacInnes and Cowperthwaite, *J. Am. Chem. Soc.*, **53**, 555 (1931). The data for benzoic acid are given by Auerbach and Smolczyk, *Z. phys. Chem.*, **110**, 65 (1924).

Two titration curves for benzoic and acetic acids, acids of nearly equal strength, are illustrated in Fig. 5. In the case of the acetic acid titration the volume at the end point was about 18 cc. while in the case of the benzoic acid the volume was 58 cc. Increase of volume diminishes the change in pH per increment of base

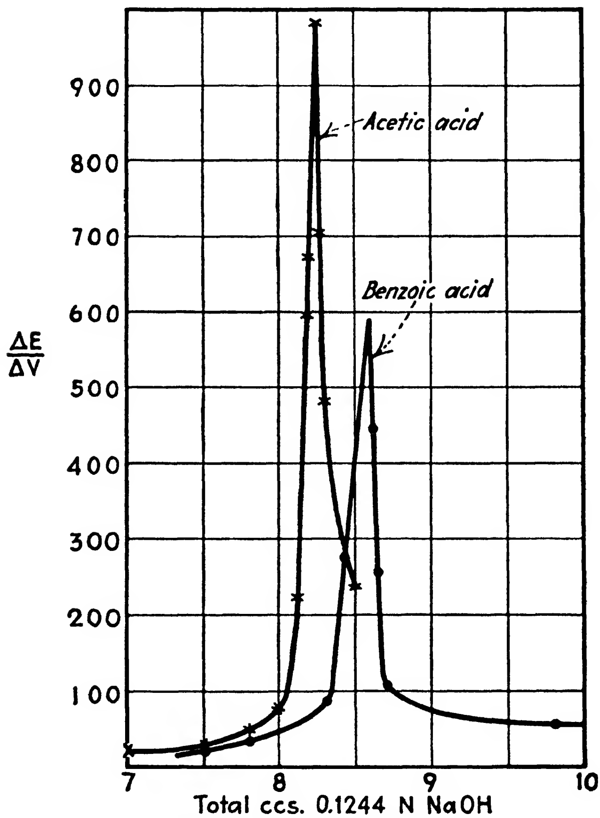


Fig. 5.

at the end point and so diminishes the maximum.* If the amount of base added in each addition is increased, the maximum will increase in height. The error in finding the end point, however, is smaller, the more dilute is the added base. In

* These data were also taken from Auerbach and Smolczyk, *loc. cit.* The maxima do not coincide because different amounts of acid were taken for titration in the two cases.

practice it is customary to dilute the titrating reagent to as low a concentration as possible, but if it is diluted too much, the curve will be flattened out and no maximum will appear.

The theory of potentiometric acid-base titrations has recently been considered by Auerbach and Smolczyk, Eastman, and Roller.* In the titration of a weak acid with a strong base it is possible to calculate the hydrogen ion concentration at any point of the titration preceding the end point by the so-called Henderson-Hasselbach equation.

$$\mathrm{pH} = \mathrm{p}K_A + \log \frac{c_{salt}}{c_{acid}}. \tag{12}$$

The dissociation constant of the weak acid, HA, is given by the equation (omitting activity coefficients)

$$K_A = \frac{c_{H^+} \cdot c_{A^-}}{c_{HA}}$$

or

$$c_{H^+} = K_A \cdot \frac{c_{HA}}{c_{A^-}}. \tag{13}$$

On the acid side of the end point it can be assumed that the weak acid is very little dissociated; in this case we can write

$$c_{HA} = \text{concentration of unneutralized acid} = c_{acid}. \tag{14a}$$

and

$$c_{A^-} = \text{concentration of salt resulting from added base} = c_{salt}. \tag{14b}$$

Introducing Eqs. (14a) and (14b) into Eq. (13), then Eq. (12) is immediately obtained. When the acid is half neutralized,

$$c_{salt} = c_{acid}.$$

and

$$\mathrm{pH} = \mathrm{p}K_A. \tag{15}$$

Hence it is possible to calculate dissociation constants from titration curves provided the e.m.f. is measured over the range

* AUERBACH and SMOLCZYK, *Z. phys. Chem.*, **110**, 65 (1924); E. D. EASTMAN, *J. Am. Chem. Soc.*, **47**, 332 (1925); P. S. ROLLER, *ibid.*, **50**, 1 (1928); **54**, 3485 (1932). See also the books by KOLTHOFF and FURMAN, "Potentiometric Titrations," 1926 and "Volumetric Analysis," Vol. I, John Wiley & Sons, Inc., New York, 1928.

corresponding to 50 per cent neutralization. This method of determining dissociation constants finds widespread application.

Eastman gives an exact equation for the concentration of the hydrogen ion at the end point, but as the equation is biquadratic in c_{H^+} it is impossible to solve it. Roller, however, has derived an approximate equation for the hydrogen ion concentration at the inflection point and compared this equation with a similar one for the hydrogen ion concentration at the stoichiometrical equivalence point. He finds that the electrometric end point coincides with the true end point except for very weak acids. But in the case of very weak acids, $K_A = 1 \times 10^{-10}$ or less, it is practically impossible to locate the electrometric end point; hence we can conclude that the potentiometric method of analysis gives us sufficiently accurate results.

Titration of Dibasic Acids or Mixtures of Two Acids.—The titration of dibasic acids or mixtures of two acids sometimes results in two inflection points in the titration curve and sometimes in only one inflection point. If the two acids are of nearly the same strength or if the first and second dissociation constant of a dibasic acid do not differ too greatly, the titration of the two acids will result in only one inflection point, or in only one maximum if the data are plotted differentially. In a mixture of a strong and weak acid the strong acid can be titrated separately from the weak acid provided the weak acid is not appreciably dissociated at the end point of the strong acid titration. Britton* states that the dissociation constant of the stronger acid must be 10,000 times the dissociation constant of the weaker acid in order for two end points to appear. In the case of sulfuric acid only one end point results on titration, but in the case of chromic acid, H_2CrO_4, two end points appear. Data for chromic acid obtained by Britton† are plotted in Fig. 6. The first dissociation of chromic acid is fairly complete, but the dissociation constant of the second dissociation is of the order of magnitude of 10^{-7}. The first end point occurs at a pH of 4.3 which means that the solution is still acid enough to repress the second dissociation of the chromic acid.

* H. T. S. Britton, "Hydrogen Ions," D. Van Nostrand Company, Inc., New York, 1929.

† H. T. S. Britton, *J. Chem. Soc.*, **125**, 1572 (1924).

Glasstone* points out that a satisfactory idea of the complete neutralization curve for a mixture of acids may be obtained, in most cases, by plotting the curves for the two acids separately side by side and then connecting them by their common tangent.

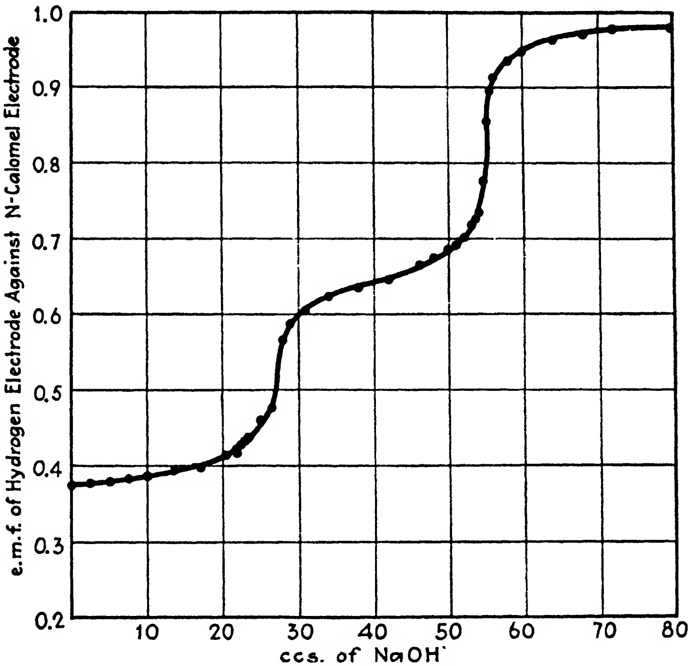


FIG. 6.—Titration of 100 cc. 0.02475 M H_2CrO_4 with 0.09 N NaOH.

Precipitimetric Titrations.—Lange and Schwartz† have made an interesting theoretical and experimental study of the potentiometric titration of silver solutions with chloride solutions. In a solution saturated with silver chloride the following equation is valid:

$$c_{Ag^+} \cdot c_{Cl^-} \cdot f_{Ag^+} \cdot f_{Cl^-} = L. \tag{16}$$

If

$$c_{Ag^+} \cdot c_{Cl^-} = L_c, \tag{17}$$

* S. GLASSTONE, "The Electrochemistry of Solutions," p. 200, Methuen & Co., Ltd., London, 1930.

† E. LANGE and E. SCHWARTZ, *Z. phys. Chem.*, **129**, 111 (1927); see also HAHN and FROMMER, *Z. phys. Chem.*, **127**, 1 (1927).

then

$$L_c \cdot \mathrm{f}_{\mathrm{Ag}^+} \cdot \mathrm{f}_{\mathrm{Cl}^-} = L. \tag{18}$$

L_c is the usual solubility product constant; it is not, however, independent of the ionic strength of the solution. Lange and Schwartz's method of handling the theoretical aspects of the titration is to consider the effect of adding small amounts of chloride or silver ions to the solution which already contains these ions in equivalent amounts, *i.e.*, to the solution at the equivalence point. Let V equal the volume of the solution in liters, P the total amount of silver ions added, and p the amount of silver added in single portions, (both p and P expressed in moles). If Δc_{Ag^+} is the increase in silver ion concentration and Δc_{Cl^-} the increase in chloride ion concentration, we can then write Eq. (17)

$$(\sqrt{L_c} - \Delta c_{\mathrm{Cl}^-})(\sqrt{L_c} + \Delta c_{\mathrm{Ag}^+}) = L_c; \tag{19}$$

also

$$P = V \cdot \Delta c_{\mathrm{Cl}^-} + V \cdot \Delta c_{\mathrm{Ag}^+}. \tag{20}$$

Eliminating Δc_{Cl^-} from Eqs. (19) and (20)

$$-\sqrt{L_c} \cdot \frac{P}{V} + 2\Delta c_{\mathrm{Ag}^+} \cdot \sqrt{L_c} - \frac{P}{V} \cdot \Delta c_{\mathrm{Ag}^+} + \Delta c^2_{\mathrm{Ag}^+} = 0, \tag{21}$$

or

$$\Delta c_{\mathrm{Ag}^+} = -\frac{1}{2}\left(2\sqrt{L_c} - \frac{P}{V}\right) + \sqrt{L_c + \frac{P^2}{4V^2}}. \tag{22}$$

Equation (22) gives the increase in concentration of silver ions on adding P moles of silver nitrate to a solution which is at its equivalence point. The e.m.f. of a silver electrode immersed in the solution is given by the equation

$$E = \frac{RT}{F} \ln \frac{c''_{\mathrm{Ag}^+} \cdot \mathrm{f}''_{\mathrm{Ag}^+}}{c'_{\mathrm{Ag}^+} \cdot \mathrm{f}'_{\mathrm{Ag}^+}}. \tag{23}$$

If we assume that the activity coefficient of the silver ion does not change on adding P moles of silver nitrate, Eq. (23) can be written

$$E = \frac{RT}{F} \ln \frac{c_{\mathrm{Ag}^+} + \Delta c_{\mathrm{Ag}^+}}{c_{\mathrm{Ag}^+}}. \tag{24}$$

introducing the value of Δc_{Ag^+} given by Eq. (22) into Eq. (24), we obtain

$$E = \frac{RT}{F} \ln \left[\frac{P}{2V\sqrt{L_c}} + \sqrt{1 + \frac{P^2}{4V^2L_c}} \right], \tag{25}$$

remembering that at the end point $c^2_{Ag^+} = L_c$. We are more interested, however, in the change of E per single addition of silver nitrate than we are in the total change of E per total amount of silver nitrate added. Differentiating Eq. (25)

$$dE = \frac{RT}{F} \cdot \frac{dP}{\sqrt{4V^2L_c + P^2}}. \tag{26}$$

At the end point P equals zero; hence the maximum in the differential e.m.f. curve is given by the equation

$$\Delta E_{max.} = \frac{RT}{F} \cdot \frac{p}{2V\sqrt{L_c}} \tag{27}$$

or, since $\sqrt{L_c} = \frac{\sqrt{L}}{\text{f}_\pm}$

$$\Delta E_{max.} = \frac{RT}{F} \frac{p\text{f}_\pm}{2V\sqrt{L}} \tag{28}$$

Equation (28) is interesting inasmuch as it tells us that the observed maximum in e.m.f. is greater the larger are the separate portions of titer added, *i.e.*, the maximum will be twice as great if twice as much silver nitrate is added. The maximum is also greater if the solubility product is lowered; this may be accomplished by lowering the temperature (Lange and Schwartz point out that for this reason it is necessary to carry out the silver chloride titration at zero degree). The maximum is also inversely proportional to the volume of the solution; this fact has already been demonstrated in the case of the acid-base titration (Fig. 5). Finally, the maximum potential difference diminishes as the mean activity coefficient of the silver chloride diminishes. Since the presence of neutral salt lowers the activity coefficient (as predicted by the equations of Debye and Hückel and as found by experiment), it is obvious that the titration of a 0.1 N solution will yield a lower e.m.f. maximum than the titration of a 0.01 N solution other factors being equal. Figure 7, taken from Lange and Schwartz's paper, illustrates the effect of neutral salt upon the e.m.f. maximum.

Differential Potentiometric Titrations.—It is possible to carry out a potentiometric titration in such a way that ΔE instead of E

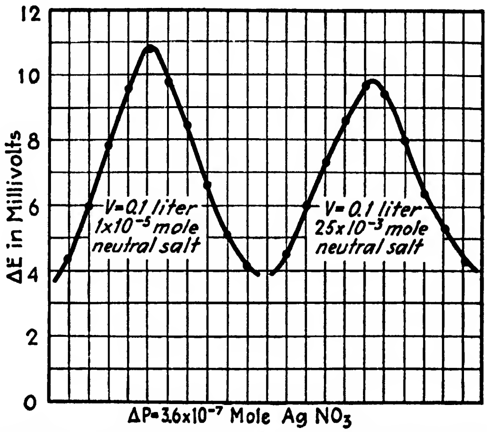


FIG. 7.—Influence of neutral salt upon the differential titration curve.

is measured at each point of the titration. This differential method, initiated by Cox,* has been chiefly developed by MacInnes† and coworkers. A convenient differential titration cell is illustrated in Fig. 8. E and E' represent two identical electrodes immersed in the solution to be titrated. Acid-base, oxidation-reduction and precipitimetric titrations may be carried out in the apparatus. The solution in the main part of the beaker is carried into the small titration cell H by means of the air lift pump L. When the solution has become uniform the difference in e.m.f., ΔE, between the two electrodes should be zero. If,

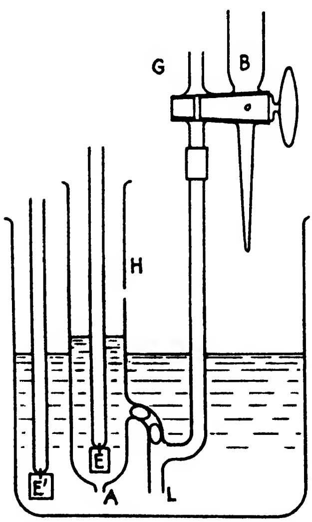


FIG. 8.—Differential potentiometric titration cell.

* Cox, *J. Am. Chem. Soc.*, **47**, 2138 (1925).

† D. A. MACINNES and P. T. JONES, *J. Am. Chem. Soc.*, **48**, 2831 (1926); MACINNES, *Z. physik. Chem.*, **130**, 217 (1927); MACINNES and DOLE, *J. Am. Chem. Soc.*, **51**, 1119 (1929); MACINNES and COWPERTHWAITE, *ibid.*, **53**, 555 (1931).

however, the stopcock of the burette *B* is turned in such a direction that the air supply is cut off at *G* and a definite amount of reagent added, the concentration of the solution outside the little titration cell is altered while that inside the cell remains constant. A potential difference ΔE now exists and can be measured. After the measurement of the e.m.f. the two solutions are again mixed by the air lift pump and the whole procedure repeated. At the end point the difference in potential ΔE is a maximum as illustrated in Figs. 4, 5, and 7. This scheme of titration has the advantage of doing away with the troublesome salt-bridge and reference electrode; the whole apparatus can be made very compact.

Exercises

1. One hundred cubic centimeters of 0.01277*c* H_3PO_4 were titrated with 0.0919 *N* NaOH at 20°C. with the hydrogen electrode *N* calomel electrode combination yielding the data of Table II. Plot *E* versus cubic centimeters of NaOH added, also $\frac{\Delta E}{\Delta \text{ cc. NaOH}}$ versus cubic centimeters of NaOH added. Compute cubic centimeters of NaOH necessary to neutralize one-third of the H_3PO_4, two-thirds of the H_3PO_4, and the whole of the H_3PO_4.

TABLE II.—TITRATION OF H_3PO_4 WITH NaOH

NaOH, cc.	*E*	NaOH, cc.	*E*
0.0	0.408	26.0	0.731
2.55	0.416	27.0	0.751
5.0	0.423	27.5	0.773
7.5	0.433	29.0	0.883
10.0	0.447	30.0	0.909
11.0	0.455	31.0	0.921
12.0	0.464	32.0	0.928
13.0	0.486	34.0	0.940
13.5	0.521	36.0	0.949
14.5	0.610	38.0	0.954
15.0	0.625	40.0	0.959
16.0	0.640	42.5	0.964
17.5	0.657	45.0	0.968
20.0	0.675	47.5	0.973
22.5	0.695	50.0	0.975
25.0	0.719		

2. Estimate the first, second and third dissociation constants of phosphoric acid. The pH can be calculated from the equation

$$\mathrm{pH} = \frac{E - 0.283}{0.0577}.$$

3. A mixture of 25 cc. 0.1 N HCl, 10 cc. 0.3c H_2SO_4 and 35 cc. of 0.5 N *o*-nitrophenol ($K_A = 5.6 \times 10^{-8}$) were titrated with 0.1 N NaOH differentially. Calculate the number of cubic centimeters of NaOH added at each moment that the $\Delta E/\Delta V$ curve reaches its maxima.

CHAPTER XXV

THE GLASS ELECTRODE

In recent years considerable interest has developed in a new type of hydrogen electrode, the glass electrode. Since the glass electrode has not been adequately discussed in older electrochemical texts, it seems worthwhile to devote a short chapter to it here.

At the phase boundary between a glass wall and an aqueous solution a potential is produced which is a function of the hydrogen ion concentration of the solution. This was discovered by the biologist, Cremer, but it was Haber and Klemensiewicz* who first made a systematic experimental study of the glass electrode.

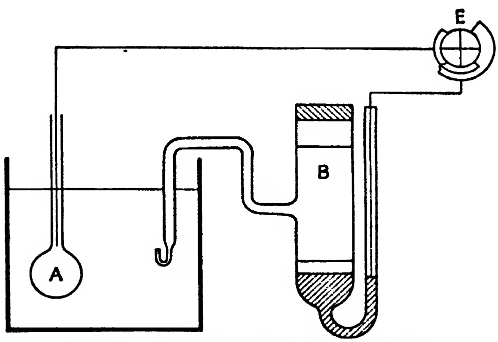


FIG. 1.—Haber's glass electrode cell.

Haber's cell is illustrated in Fig. 1. The glass electrode *A* was blown from soft glass into the form of a thin bulb, several hundredths of a millimeter thick. An acid solution was placed inside the bulb and the bulb immersed in the solution in the beaker. The reference half cell *B* is a calomel electrode and the circuit is completed through the electrometer *E*. Haber and Klemensiewicz showed that the e.m.f. of the cell varied with

* M. CREMER, *Z. Biologie*, **47**, 562 (1906); F. HABER and Z. KLEMENSIEWICZ, *Z. physik. Chem.*, **67**, 385 (1909).

change of acid concentration of the solution in the beaker in the manner expected of the ordinary hydrogen electrode. This was accomplished without the presence of hydrogen gas.

Haber's remarkable results stimulated considerable interest in the glass electrode not only because of the theory involved, but also because of the possibility of using the glass electrode to

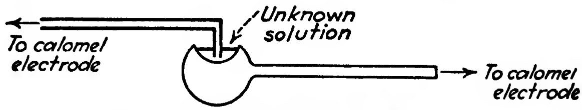


Fig. 2.—Mrs. Kerridge's glass electrode.

measure pH values. Biologists were the first to seize upon the glass electrode for practical reasons, for they had long needed an accurate instrument for measuring the pH of dye solutions, plant and animal fluids, blood, etc., solutions whose pH values could not be determined or were not conveniently determined by the use of either the quinhydrone or hydrogen electrodes. Mrs. Kerridge's* glass electrode for small quantities of fluid is shown in Fig. 2. The unknown solution is put into the little cup on top

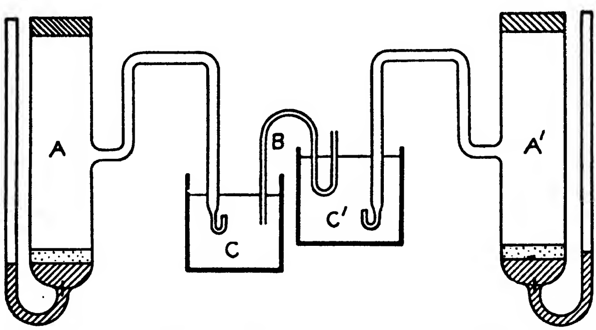


Fig. 3.—Capillary glass electrode of Youden and Dobroscky.

of the bulb, then it is connected to a calomel electrode and the e.m.f. measured. For quantities of fluid of the order of 0.01 cc. Youden and Dobroscky† invented a capillary glass electrode, Fig. 3. The unknown fluid is allowed to run into the narrow

* P. M. T. Kerridge, *Biochem. J.*, **19**, 611 (1925); *J. Sci. Instruments*, **3**, 404 (1926).

† W. J. Youden and I. D. Dobroscky, *Contributions from Boyce Thompson Institute*, **3**, 347 (1931).

capillary tube B which has a volume of 0.01 cc. or less. On closing the circuit the current flows from the calomel electrode A through some reference solution C into the glass capillary B. In the upper dish the current must flow through the walls of the glass capillary to get into the solution C' from which it flows to the calomel electrode A'.

A somewhat similar electrode has been designed by MacInnes and Belcher* (Fig. 4). The principle of this electrode is the same as the capillary electrode of Youden, but the capillary is blown in spiral form and sealed into the apparatus. The electrical resistance of the electrode is comparatively low and it is not easily broken.

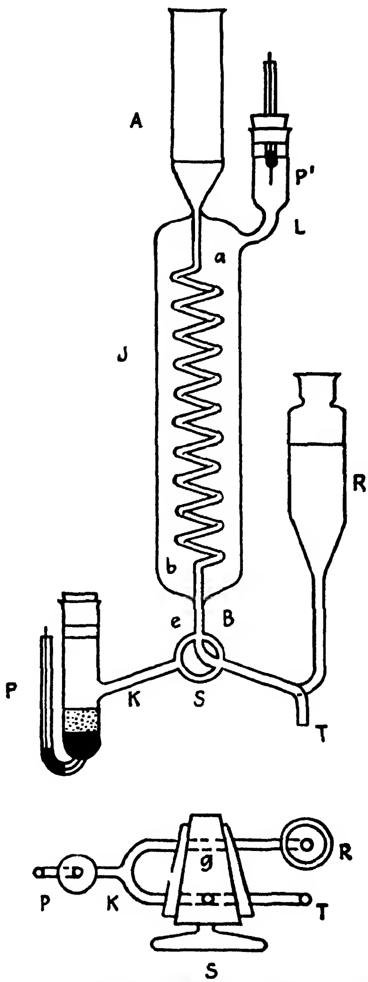


Fig. 4.—MacInnes and Belcher glass electrode.

All the glass electrodes described up to this point are fairly thick-walled. MacInnes and Dole† designed a glass electrode having walls which were only a few microns (one micron = 0.001 mm.) thick. Their electrode, illustrated in Fig. 5, consists of a piece of tubing of ordinary soft glass B on which a very thin membrane D is sealed. The sealing on of the membrane is accomplished very easily by blowing out a large, thin bubble of glass, and then heating the end of B up to dull red heat and

* D. A. MacInnes and D. Belcher, *Ind. Eng. Chem., Anal. Ed.*, **5**, 199 (1933).

† D. A. MacInnes and M. Dole, *Ind. Eng. Chem., Anal. Ed.*, **1**, 57 (1929).

plunging it onto the bulb of glass. The heat in the tube B is sufficient to fuse the thin membrane onto it. The membranes are usually made so thin that red and green diffraction colors can be seen. The glass electrode is partially filled with a reference solution such as 0.1c hydrochloric acid and the silver chloride electrode C inserted.

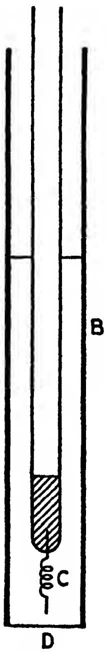


FIG. 5.—The MacInnes and Dole glass electrode.

MacInnes and Dole* also made a study of the composition of glasses used in glass electrodes in order to find out the most suitable glass. The criterion of a good glass seems to be first, low electrical resistance, and second, ability to act as a perfect hydrogen electrode over as great a pH range as possible. The glass which best meets these requirements has the formula 72 per cent SiO_2, 6 per cent CaO, and 22 per cent Na_2O; it is the lowest melting glass that can be prepared using these three ingredients. The electrical resistance of a MacInnes and Dole glass electrode of 5 mm. internal diameter is 10 million ohms (10 megohms) when made of the best glass, whereas with ordinary soft glass the resistance is ten times as great. Ssokolov and Passynsky† have recently investigated the behavior of glass electrodes made from glass having various compositions. They find that a lithium glass composed of 80 per cent SiO_2, 10 per cent CaO, and 10 per cent Li_2O is the best for alkaline solutions containing either sodium or potassium ions, but it is not so suitable for alkaline solutions containing lithium ions. It is difficult to decide from the data whether this lithium glass of Ssokolov and Passynsky is to be preferred to the sodium glass recommended by MacInnes and Dole.

In order to calculate the pH from glass electrode measurements, the glass electrode may first be standardized by measuring the pH of a known solution or the calculation may be carried out in the following manner: If both surfaces of the glass membrane act like hydrogen electrodes, the e.m.f. of the cell (A)

* D. A. MacInnes and M. Dole, *J. Am. Chem. Soc.*, **52**, 29 (1930).

† S. I. Ssokolov and A. H. Passynsky, *Z. physik. Chem.*, **A 160**, 366 (1932).

$$\text{Ag} \mid \text{AgCl} \mid \begin{array}{c}0.1\ c\\ \text{HCl}\end{array} \mid \text{glass} \mid \text{soln. X} \parallel \begin{array}{c}\text{KCl}\\ \text{sat.}\end{array} \mid Hg_2Cl_2 \mid \text{Hg} \qquad (A)$$

is equal to the e.m.f. of the cell (*B*)

$$\text{Ag} \mid \text{AgCl} \mid \begin{array}{c}0.1\ c\\ \text{HCl}\end{array} \mid H_2,\ \text{Pt-Pt},\ H_2 \mid \text{soln. X} \parallel \begin{array}{c}\text{KCl}\\ \text{sat.}\end{array} \mid Hg_2Cl_2 \mid \text{Hg} \qquad (B)$$

The e.m.f. of the cell

$$\text{Ag} \mid \text{AgCl} \mid \begin{array}{c}0.1\ c\\ \text{HCl}\end{array} \mid H_2,\ \text{Pt}$$

at 25°C. is −0.3524 v.,* while the e.m.f. of the cell

$$\text{Pt},\ H_2 \mid \text{soln. X} \parallel \begin{array}{c}\text{KCl}\\ \text{sat.}\end{array} \mid Hg_2Cl_2 \mid \text{Hg}$$

is

$$E = 0.2458 - 0.05915 \log m_{H^+} \cdot \gamma_{H^+}.$$

The total e.m.f. of the glass electrode cell (*A*) is, therefore,

$$E = -0.1066 - 0.05915 \log m_{H^+} \cdot \gamma_{H^+},$$

and the equation for the pH is

$$\text{pH} = \frac{E + 0.1066}{0.05915} \qquad (1)$$

[compare Eq. (XXIV-5)].

MacInnes and Belcher† have recently published some glass

TABLE I.—GLASS ELECTRODE pH MEASUREMENTS

Electrode	E.m.f.	Asymmetry potential	pH
R 23	0.1278	+0.0013	3.980
R 13	0.1276	0.0015	3.980
R 14	0.1278	0.0014	3.981
R 20	0.1283	0.0008	3.980
R 22	0.1284	0.0008	3.981
R 8	0.1309	−0.0017	3.981

electrode pH measurements which we may quote as a good example of the accuracy of the glass electrode. The Clark rocking hydrogen cell (Chap. XXIV) gave 3.983 for the pH of this

* G. SCATCHARD, *J. Am. Chem. Soc.*, **47**, 641 (1925).

† D. A. MACINNES and D. BELCHER, *J. Am. Chem. Soc.*, **53**, 3315 (1931).

solution. In Table I, the asymmetry potentials are the potentials given by the following cell,

$$\begin{array}{c|c|c|c|c|c|c}\mathrm{Ag} & \mathrm{AgCl} & 0.1\,c & \text{glass} & 0.1\,c & \mathrm{AgCl} & \mathrm{Ag}. \\ & & \mathrm{HCl} & & \mathrm{HCl} & & \end{array} \qquad (C)$$

If both surfaces of the glass electrode acted alike, the e.m.f. of cell (C) would be zero. In most cases the e.m.f. is nearly zero.

MacInnes and Belcher made their e.m.f. measurements in the usual way except that a Compton quadrant electrometer replaced the galvanometer of the potentiometer circuit. Glass electrode e.m.fs. have also been measured using vacuum-tube potentiometers as null-point instruments.*

The advantages of the glass electrode over the quinhydrone or hydrogen electrode are: first, the observed e.m.f. is absolutely independent of any oxidation-reduction potentials; second, it is not necessary to add hydrogen gas or quinhydrone to the unknown solution; third, it is possible to measure the pH of very small quantities of fluid; fourth, the glass electrode can be used in colored or turbid solutions; fifth, the glass electrode gives correct results in unbuffered solutions and in solutions near the neutral point; sixth, the glass electrode comes to equilibrium immediately so that pH measurements can be made very rapidly.

The experimental disadvantages of the glass electrode are its fragility and its high electrical resistance. These difficulties can be overcome, but there are serious limitations to the glass electrode that seem to be inherent in the nature of the glass itself and for that reason cannot be circumvented.

Horovitz and his coworkers and Hughes† investigated the potentials of the glass electrode in solutions containing positive ions other than the hydrogen ion, and obtained very interesting results. They proved conclusively that the glass electrode does not act like a perfect hydrogen electrode in alkaline solutions,

* Elder and Wright, *Proc. Nat. Acad. Sci.*, **14**, 936 (1928); *J. Am. Chem. Soc.*, **51**, 3266 (1929); Partridge, *J. Am. Chem. Soc.*, **51**, 1 (1929); Stadie, *J. Biol. Chem.*, **83**, 477 (1929); Fosbinder, *J. Phys. Chem.*, **34**, 1294 (1930); Morton, *J. Chem. Soc.*, **1931**, 2983; E. C. Gilbert and Alan Cobb, *Ind. Eng. Chem., Anal. Ed.*, **5**, 69 (1933).

† K. Horovitz, *Z. Physik*, **15**, 369 (1923); *Sitzb. Akad. Wiss. Wien, Abt. IIa*, **134**, 335 (1925); *Z. physik. Chem.*, **115**, 424 (1925); H. Schiller, *Ann. Physik*, (4) **74**, 105 (1924); W. S. Hughes, *J. Chem. Soc.*, **1928**, 491.

but gives e.m.f. values that are functions of the concentration of sodium, lithium, potassium, silver, etc., ions present in the solution. In acid solutions, where the hydrogen ion concentration is considerably higher than in basic solutions, the glass-electrode potential responds solely to changes in hydrogen ion concentration. Obviously, the glass electrode does not measure the correct pH value in alkaline solutions. The author has carried out a systematic study of the deviation of the glass electrode from the theoretical hydrogen electrode. This deviation, called

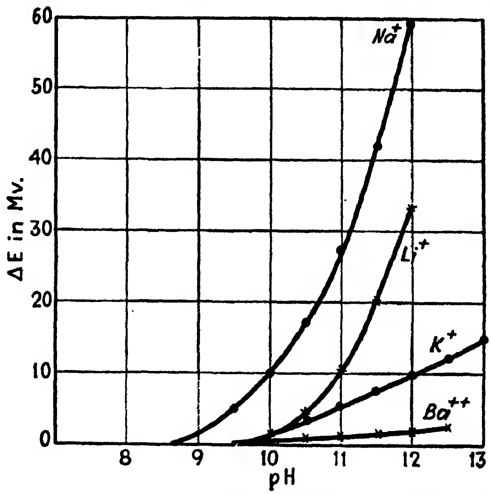


FIG. 6.—Errors of the glass electrode in 1 N solutions.

the error of the glass electrode, was measured as the pH changed in solutions of constant sodium, lithium, potassium, or barium ion concentration. The results are given in Table II and are plotted for 1.0 N solution in Fig. 6. The errors are positive; *i.e.*, the glass electrode gives more positive potentials than it should give, making the total e.m.f. of the cell

$$\overset{(-)}{Ag} \,\Big|\, AgCl \,\Big|\, \begin{matrix} 0.1\ c \\ HCl \end{matrix} \,\Big|\, glass \,\Big|\, \begin{matrix} basic \\ solution \end{matrix} \,\Big\|\, \overset{(+)}{Calomel}$$

less than it should be as the basic solution becomes more basic. It is interesting to note the marked difference in behavior of the glass electrode in the different solutions. The error is so slight in barium solutions that the pH can be determined in these

solutions nearly exactly. Negative ions have apparently no effect upon the e.m.f.* Large organic ions also cause the glass electrode to be very little in error.

TABLE II.—ERRORS OF THE GLASS ELECTRODE IN AQUEOUS SOLUTIONS AT 25°C.
(Millivolts)

pH	0.1 *c* LiOAc	1.0 *c* LiOAc	0.05 *c* Na_2HPO_4	1.0 *c* Na^+	0.1 *c* KOAc	1.0 *c* KOAc	0.5 *c* $Ba(OAc)_2$
9.5	0.5	0	1.6	5.0	0.8		
10.0	1.5	1.2	3.4	9.8	1.5	1.8	0.5
10.5	3.0	4.6	6.0	17.2	2.5	3.3	0.8
11.0	5.3	10.6	10.8	27.2	3.6	5.2	1.1
11.5	8.6	20.2	16.4	42.0	4.9	7.2	1.4
12.0	...	33.3	24.3	59.2	6.2	9.6	1.7
12.5	...	....	....	....	...	12.0	2.1
13.0	...	....	....	....	...	14.6	

The symbol OAc refers to the acetate ion.

The alkaline solution potentials of the glass electrode are stable and reproducible, provided the proper glass is used. Different types of glasses give different potentials in alkaline solutions; as a general rule it may be said that hard glasses act less like a hydrogen electrode and more like a sodium (or potassium, etc.) electrode in alkaline solutions.

In acid solutions the glass electrode functions without error, but in very acid solutions, it begins again to deviate from its theoretical hydrogen electrode values, as MacInnes and Belcher† first discovered. The behavior of the glass electrode in acid aqueous and nonaqueous solutions has been studied most extensively by the author.‡ The errors here are negative in sign; *i.e.*, the glass electrode gives more negative potentials than it should give, making the total e.m.f. of the cell

(+) Ag	AgCl	0.1 *c* HCl	glass	acid solution ‖	(−) calomel

* M. DOLE, *J. Am. Chem. Soc.*, **53**, 4260 (1931).

† MACINNES and BELCHER, *J. Am. Chem. Soc.*, **53**, 3315 (1931); see also BUCHBÖCK, *Z. physik. Chem.*, **A 156**, 232 (1931).

‡ M. DOLE, *J. Am. Chem. Soc.*, **54**, 3095 (1932).

less than it should be as the acid solution becomes more acidic. In other words the total e.m.f. of the two phase boundaries

Inside solution	glass	outside solution

cannot become large in the direction either of acidic solutions or of basic solutions. Errors of the glass electrode in hydrochloric acid solutions are plotted in Fig. 7, and it can be seen that below a pH of zero (1 N HCl) the errors become negative. The glass electrode also gives negative errors in acid solutions of ethyl alcohol and in neutral aqueous solutions if the salt concentration is very high (4 N LiCl, for example). Apparently the glass electrode may be used to measure the pH accurately only in aqueous solutions between pH values of zero and nine.

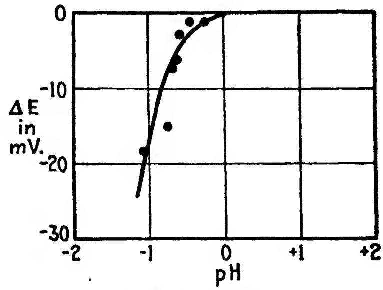
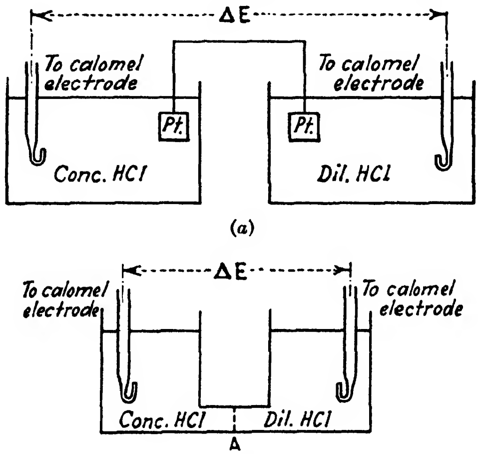


FIG. 7.—Errors of the glass electrode in hydrochloric acid.

The Theory of the Glass Electrode.—Any theory of the glass electrode must account for its behavior in alkaline solutions, in very acid solutions and in neutral solutions. In neutral solutions, where the glass electrode acts as a hydrogen electrode, thermodynamics gives a perfectly clear explanation. Imagine two hydrochloric acid solutions of different concentrations in which two hydrogen platinum electrodes are immersed (Fig. 8*a*). As one faraday of current flows through the cell, one equivalent of hydrogen ions is reversibly transferred from the concentrated to the dilute solution, and the free energy of transfer, measured by the e.m.f. (with neglect of liquid-junction potentials), is equal to the difference in free energy of the hydrogen ion in the two solutions. Consider the analogous glass electrode system (Fig. 8*b*) with the glass electrode at A. As one faraday of current flows through the glass electrode, one equivalent of hydrogen ions is reversibly transferred from the concentrated to the dilute solution, and, although the mechanism of the process is entirely different from that of the hydrogen electrode, the net result is

exactly the same, the free-energy change is exactly the same and therefore the e.m.f. of the glass electrode system must be exactly the same as that of the hydrogen electrode system. Thermodynamics is not concerned with the manner in which the transfer is carried out; thermodynamics deals only with the difference in energy between the final and initial states of the system. The equation for the e.m.f. across the glass membrane may be derived thermodynamically from any liquid-junction-potential equation by setting the mobility of the negative ion equal to zero, from



(a) (b)

Fig. 8.

the Gibbs-Donnan semipermeable-membrane equation by assuming that the glass is permeable only to hydrogen ions, and from the phase-boundary equations by assuming that the hydrogen ion concentration in the glass remains constant. A little reflection will show that these three assumptions are physically equivalent. The equation obtained is, of course, the same as that of the hydrogen electrode (with opposite sign)

$$E = \frac{RT}{F} \ln \frac{c'_{H^+} \cdot f'_{H^+}}{c''_{H^+} \cdot f''_{H^+}}.$$

It is interesting to compare the mechanisms of the hydrogen and glass electrode processes. In the case of the hydrogen electrode, hydrogen ions capture electrons or neutral hydrogen atoms lose electrons as the current flows, but the mechanism of the glass

electrode is quite different. In the case of the glass electrode we believe that the hydrogen ion passes through the glass as an ion and never gains an electron to become neutral hydrogen. Because the hydrogen ion does not react with an electron as the current flows through the glass, the glass electrode potential is uninfluenced by oxidation-reduction potentials in the solution. The platinum surface of a hydrogen electrode is affected by the electron transfer of an oxidation-reduction reaction, and therefore the ordinary hydrogen electrode cannot be used to measure hydrogen ion concentration in the presence of oxidation-reduction reactions.

Experimental proof of the assumption that only hydrogen ions migrate through glass as the current flows has been obtained by Quittner.*

The foregoing explanation of the glass electrode is valid only for aqueous solutions between the pH values 0 and 9. In very acid solutions the glass electrode gives negative deviations from the theoretical hydrogen electrode equation. Since these errors did not seem to depend upon the presence or concentration of any ion in particular, but did depend upon a change in the concentration of the water, the author was able to derive the following equation for the error of the glass electrode in acid or nonaqueous solutions:

$$\Delta E = \frac{RT}{F} \ln \frac{c'_{H_2O} \cdot \mathbf{f}'_{H_2O}}{c''_{H_2O} \cdot \mathbf{f}''_{H_2O}}. \tag{2}$$

This equation depends upon the assumption that the hydrogen ion migrates through glass not as an unhydrated hydrogen ion (the proton) but as a hydrogen ion with one molecule of water of hydration. It is obvious that if the product $c_{H_2O} \cdot \mathbf{f}_{H_2O}$ is the same on both sides of the glass membrane, Fig. 8*b*, there will be no change in free energy of the water as it is transported from one solution to the other, but if the concentration or activity coefficient of the water is materially reduced by adding concentrated acid, alcohol, or a large amount of salt, there will be a free-energy change of the water as the current flows. This free-energy change which is not present in the case of the hydrogen electrode should appear in the e.m.f.; hence, if water is carried through the glass, thermodynamics tells us that the glass

* F. Quittner, *Ann. Physik*, (4) **85**, 745 (1928).

electrode will not give the same e.m.f. as the hydrogen electrode.

The author has tested Eq. (2) quantitatively and has found it verified within the experimental uncertainties of the glass electrode.* In Fig. 9, the errors of the glass electrode are plotted against the logarithm of the product $c_{H_2O} \cdot f_{H_2O}$ in a number of solutions. According to Eq. (2) a straight line should result with slope equal to 0.059 and with intercept on the x-axis equal to zero. These conditions are approximately fulfilled as can be readily seen by comparing the data with the solid line which is the theoretical curve of Eq. (2).

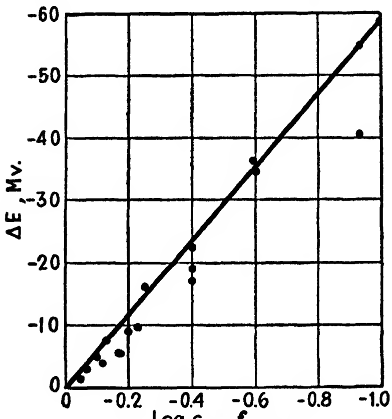


FIG. 9.—A test of Eq. (2).

It is known that glass of the composition recommended by MacInnes and Dole contains water, for if the glass electrode is dried out, the resistance increases. When the glass electrode is immersed in a nonaqueous solution, hydrogen ions migrating out of the glass may carry water with them, and hydrogen ions migrating into the glass may carry alcohol or other neutral molecules with them. Because of this fact, the glass electrode gives unstable potentials and may not be used to determine the pH of a nonaqueous solution. If it were possible to devise a glass which would allow nonsolvated hydrogen ions or protons to migrate through the membrane, it would be possible to measure the pH of nonaqueous solutions.

The theory of the alkaline solution behavior of the glass electrode has not yet been fully developed. The application of Gurney's quantum and statistical mechanical theory of electrochemistry to the glass electrode results in the following equation for alkaline solution errors of the glass electrode [Eq. XXIX-12)]:

$$\Delta E = \frac{RT}{F} \ln \frac{c_{H^+} + c_{Na^+} B e^{\frac{-A}{RT}}}{c_{H^+}}, \tag{3}$$

* M. DOLE, *J. Am. Chem. Soc.*, **54**, 2120 (1932); **54**, 3095 (1932).

where B and A are constants. Dropping out B because it is the order of magnitude of unity and rearranging Eq. (3) into an equation of a straight line, we obtain

$$\log\left[e^{\frac{F\Delta E}{RT}} - 1\right] = \log c_{Na^+} \cdot e^{\frac{-A}{RT}} + \mathrm{pH}. \qquad (4)^*$$

By plotting the left hand side of Eq. (4) against the pH, straight lines with unit slopes should result. Such a plot is illustrated

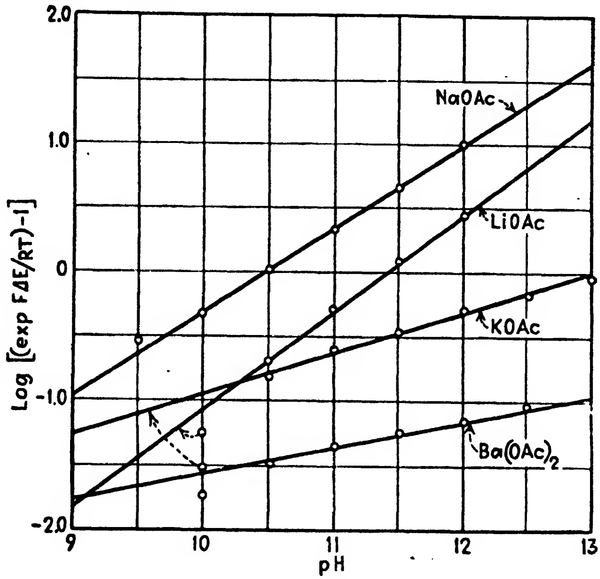


FIG. 10.—Test of Eq. (4) for 1-N salt solutions.

in Fig. 10 where straight lines are obtained, but they do not have a unit slope. However, if the constant A of Eq. (3) is not a constant, but is a function of the pH, the slopes of these curves should not be unity.

It should be pointed out that Eq. (3) was derived on the assumption that negative ions play no role in the process by which the glass electrode potential is set up. This assumption seems to be well justified since a change in nature of the negative ion present in the solution has no effect on the error of the glass electrode.

* An equation similar to Eq. (4) was first derived by Dole, *J. Am. Chem. Soc.*, **53**, 4260 (1931), on the assumption that the potential at the aqueous solution-glass interface was a liquid-junction potential.

Although a precise mathematical theory has not yet been formulated for the alkaline solution errors, it is easy to understand why the glass electrode is in error in the high pH range. In these solutions there are few hydrogen ions to carry the current across the glass-aqueous solution boundary; it is reasonable to suppose, therefore, that the other positive ions which are present in concentrations 10^9 or more times as great as the hydrogen ion carry some of the current across the boundary. If this is true, then the e.m.f. measures the free energy of transfer of other ions in addition to the hydrogen ion, and the glass electrode fails to be an electrode strictly reversible to the hydrogen ion.

Phase-boundary Potentials at Other Solid-liquid Interfaces.—Lengyel* has recently carried out some interesting experiments in which the e.m.f. of fused quartz membranes was measured. Lark-Horovitz† has also carried out similar experiments not only on quartz membranes but also on paraffin membranes. The results are somewhat analogous to those of the glass electrode. In neutral or alkaline solutions the potentials are a function of the metal ion concentration. In acid solutions, the hydrogen ion predominates so that quartz and paraffin membranes act partially as hydrogen electrodes. In very acid solutions, the deviations of the e.m.f. from the e.m.f. of a perfect hydrogen electrode are negative just as they are with the glass electrode. The theory of these membranes is not yet clear; Lengyel advocates an adsorption theory, while Lark-Horovitz believes that ionic exchange on the quartz or paraffin surface is responsible for the observed effects. It is possible that statistical mechanics may give a reasonable explanation of these potentials. Apparently the results are not accurate enough to treat them thermodynamically, as the glass electrode results have been treated.

Lengyel‡ has also carried out some interesting experiments on graphite electrodes. He has measured the potential of electrodes of pure Acheson graphite in solutions of various hydrogen, sodium, lithium, potassium, and barium chloride concentrations

* B. v. Lengyel, *Z. physik. Chem.*, **153 A**, 425 (1931); **159 A**, 145, 393 (1932).

† K. Lark-Horovitz, *Die Naturwissenschaften*, **19**, 397 (1931).

‡ B. v. Lengyel, *Z. physik. Chem.*, **154**, 371 (1931).

and discovered that quite similarly to the quartz and paraffin membranes the graphite electrode potentials vary with change of pH in acid solutions, but in neutral solutions the potential is determined by the concentration of the salt present. Barium chloride influences the potential as much as does potassium or sodium chloride. However, if some quinhydrone is added to the system, the graphite quinhydrone system immediately behaves exclusively as a quinhydrone electrode and is uninfluenced by change of salt concentration. Lengyel attributes the behavior of the graphite electrode to a cation adsorption on the surface of the graphite. One wonders why the change of potential with change of barium ion concentration is not half the change one measures with change of sodium ion concentration, as it should be according to the equation

$$E = \frac{RT}{2F} \ln \frac{c''_{Ba^{++}} \cdot f''_{Ba^{++}}}{c'_{Ba^{++}} \cdot f'_{Ba^{++}}}.$$

Between 1 N and 0.1 N sodium chloride solutions the measured e.m.f. is 0.056 v. (theoretical 0.059), and between 1 N and 0.1 N barium chloride solutions the measured e.m.f. is 0.042 v. when the theoretical e.m.f. is 0.029 v. (because barium has a valence of two).

Schmid and Winkelmann* have measured the potentials of copper electrodes against aqueous solutions containing no copper. ions with the results given in Table III. These investigators point out that a change of concentration changes the e.m.f.

TABLE III.—Cu-METAL; NORMAL-CALOMEL ELECTRODE = 0 VOLT, TEMPERATURE, 18°C., E.M.F. RESULTS

N	NaCl	KCl	KBr	KF	Na_2SO_4
5	0.380				
4	0.371	0.371	0.455	0.309	
3	0.336	0.354	0.428	0.255	
2	0.310	0.327	0.405	0.227	0.198
1	0.282	0.292	0.371	0.189	0.170
0.1	0.208	0.198	0.318	0.161	0.112
0.01	0.161	0.161	0.170	0.152	0.092

* A. SCHMID and W. WINKELMANN, *Helv. chim. Acta*, **13**, 304 (1930); **15**, 1393 (1932).

considerably and that the negative ions have a greater influence on the interfacial potential than do the positive ions.

Hitherto we have considered solid-liquid interfaces whose potentials are very definitely altered by a change in the nature and concentration of the solution in contact with the solid. It is interesting now to describe briefly a phase boundary whose potential seems to be nearly independent of the nature and concentration of the solution with which it is in contact. Kamienski* prepared some electrodes of clear green carborundum and found, in comparison to a platinum electrode, that these electrodes showed no change of potential on changing the concentration of oxidant and reductant in the system while the platinum electrode changed 0.4 v. A change in hydrogen ion concentration from a pH of 3 to a pH of 11, approximately, changed the e.m.f. by only 0.023 v.

* B. Kamienski, *Z. physik. Chem.*, **138 A**, 345 (1928); *ibid.*, **145 A**, 48 (1929).

CHAPTER XXVI

ELECTROKINETIC PHENOMENA

Introduction.—In this and the following chapter we shall study electrical phenomena which are due to or influenced by surface adsorption. Substances that are active in colloid chemistry, such as ions of high valence and certain organic compounds, affect the e.m.f. of a galvanic cell only in so far as their presence changes the activity coefficient of the ion taking part in the electrode reaction. But these **capillary active** substances may have a very great effect upon electrokinetic and electrocapillary phenomena. For example, the velocity of migration of a colloidal particle may be slowed down and in some cases the direction of its velocity may be actually reversed by the addition of small amounts of ions of high valence. Organic substances like fuchsin likewise influence electrokinetic phenomena very greatly. The study of these effects is interesting and important, not only for theoretical chemistry, but also for the practical fields of industry and biology.

While the term "electrocapillary" has frequently included all electrical effects due to adsorption, we shall define electrocapillary phenomena as electrical effects caused by the change in surface tension; more specifically, electrocapillary phenomena are limited here to the interesting potentials observed at the surface of a liquid as the surface tension of the liquid is altered. Electrokinetic phenomena are those which arise from matter in motion (hence the name electro*kinetic*). The latter may be classified as follows:

1. *Electrophoresis*, the migration of suspended solid, liquid, or gaseous colloidal particles under the influence of an external e.m.f.,

2. *Electrosmosis*, the migration of liquid past a solid surface under the influence of an external e.m.f.,

3. *Streaming e.m.f.*, e.m.f. produced by the flow of liquid past a solid surface, and finally

4. *Migration or sedimentation e.m.f.*, e.m.f. produced by particles which are moved mechanically as by the force of gravity.

Electrophoresis is by far the most important phenomenon from an industrial or biological standpoint and will, therefore, be considered first.

Electrophoresis.—A colloidal solution known as a suspensoid results from the dispersion of a chemical element or compound in some dispersion medium such as water. Although the dispersed

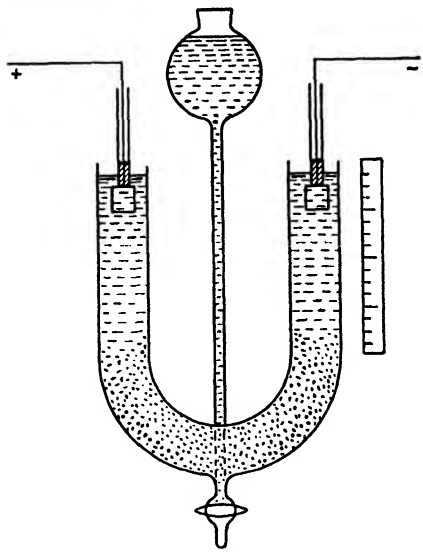


FIG. 1.—A cell for the observation of electrophoresis.

particles are formed from neutral substances, nevertheless they exhibit electrophoresis; that is, the particles migrate in a definite direction and with a definite velocity if an external e.m.f. is applied to the solution. If the boundary between the colloidal solution and the pure dispersion medium is sharp and readily visible, it is possible to observe and to measure the velocity of the boundary as it migrates under the force of the applied voltage. A simple type of apparatus, devised by Burton* is illustrated in Fig. 1. If the suspensoid happens to be a ferric hydroxide sol, the colloidal particles migrate to the negative

* E. F. BURTON, *Phil. Mag.*, (6) **11**, 425 (1906); **12**, 472 (1906); **17**, 583 (1909).

electrode as the current flows through the cell. The velocity of migration is easily measured on the scale attached to the apparatus. Accurate results are not readily obtainable, however, owing to the fact that the boundary may change its appearance during the electrolysis; furthermore the method is limited to colored sols. Svedberg and Jette* have applied this method in a very interesting fashion. They made the boundary visible by causing the colloid to fluoresce under the influence of ultraviolet light. The motion of the colloid could thereby be photographed. Svedberg and Jette applied their fluorescent method to the

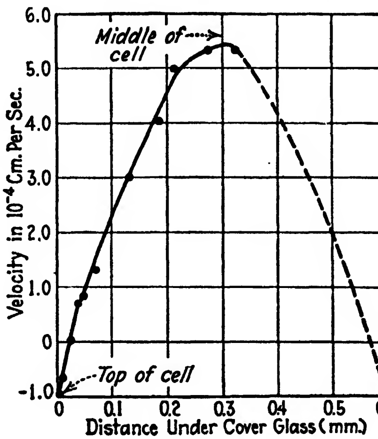


FIG. 2.

measurement of electrophoresis of colorless protein colloids. Michaelis† also was able to obtain a rough estimate of the velocity of migration of proteins by analysing the liquid in various parts of the cell after the current had passed.

A more accurate method consists in the observation of a single particle by means of the microscope. The suspensoid is placed between the slide and cover glass of the microscope; after applying the electric current, the particle migrates, and its velocity can be measured. Unless the cell is deep, the migration of the water or of the dispersion medium will cause a displacement of the particle which is not due to the electric current. This displacement, caused by electrosmosis (see below), is illustrated by Fig. 2 where

* SVEDBERG and JETTE, *J. Am. Chem. Soc.*, **45**, 954 (1923).

† MICHAELIS, *Biochem. Z.*, **16**, 81 (1908).

the velocity of the colloidal particle is plotted as a function of the position of the particle in the cell. Note that the velocity near the top of the cell is in an opposite direction to the velocity in the middle of the cell.* This additional velocity must be corrected for. Svedberg and Andersson† overcame this difficulty by using alternating current. The colloid particles respond instantaneously to rapid changes in the applied e.m.f. so that their diffraction images as seen in the ultramicroscope are drawn out into lines of light by the alternating current. Svedberg and Andersson were able to calculate the velocity of the particles by measuring the length of the lines of light and by determining the periodicity of the applied field (about 11 cycles per second).

McTaggart‡ has invented an ingenious method for measuring the electrophoretic velocity of gas bubbles suspended in a liquid. Figure 3 illustrates his apparatus; *C, C* are two platinum elec-

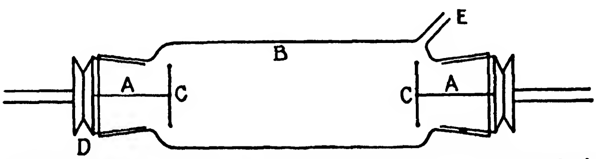


FIG. 3.—Apparatus for measuring the electrophoretic velocity of air bubbles.

trodes inserted into the cell *B* by means of the ground glass stoppers *A, A*. A pulley *D* allows the cell to be rotated at a uniform speed about its long axis in order that the gas bubble which is introduced through *E* may remain in the center of the cell. The opening at *E* is closed after the introduction of the gas bubble. By observing the horizontal motion of the air bubble its velocity is readily measured.

The question naturally arises, why do these apparently neutral substances migrate in an electric field? Although the phenomena of electrophoresis and electrosmosis had been discovered by the Russian physicist Reuss as early as 1809, it was not until 1879 that Helmholtz§ developed a mathematical theory of electro-

* R. ELLIS, *Z. physik. Chem.*, **78**, 321 (1911).

† SVEDBERG and ANDERSSON, *Kolloid. Z.*, **24**, 156 (1919); for an interesting method involving a rotating electric field, see Pugh and Swartz, *Phys. Rev.*, **36**, 1495 (1930).

‡ MCTAGGART, *Phil. Mag.*, (6), **27**, 297 (1914); **28**, 367 (1914).

§ H. HELMHOLTZ, *Ann. Phys.*, (2), **7**, 337 (1879).

kinetic phenomena. In order to explain these phenomena Helmholtz made use of the concept of an electric double layer at the surface of the colloidal particle.* Although Helmholtz's picture of the double layer has been considerably modified in recent times, his theory will be described here inasmuch as it is still accepted in its broad general outlines. Helmholtz assumed a layer of charges to exist in a thin film of the dispersion medium which was fixed to the colloidal particle and immediately adjacent to this fixed layer of charges a movable layer of charges of opposite sign contained in the dispersion medium as illustrated in Fig. 4. It has been stated several times before in this book that when two phases come into contact, an interfacial potential is produced at the boundary. Helmholtz assumed a layer of charges to exist on one phase and immediately adjacent a layer of opposite charges on the second as illustrated in Fig. 4.

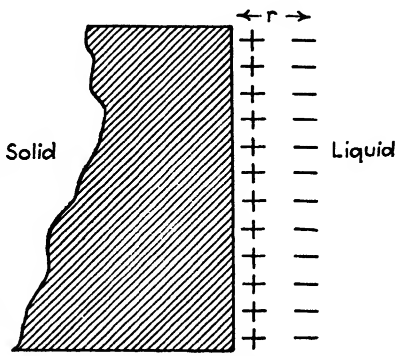


FIG. 4.—Schematic representation of the Helmholtz double layer.

Helmholtz believed that the distance between the positive and negative layers was of the order of atomic dimensions and that the potential fell abruptly at the interface. It must be realized that the net charge on any colloidal solution is zero; the charges in the fixed layer are exactly neutralized by the remaining charges in the solution. Without taking up at this point the question of the origin of the charges of the double layer, let us review briefly Helmholtz's mathematical treatment. (Smoluchowski has developed the following theory in the case of particles of any size or shape.)

When an external e.m.f. is applied to the solution, there will be an electrical force on the surface of the solid particle because the surface is charged, and there will also be an electrical force on the liquid because it is charged. The liquid and the solid will

* G. Quincke, *Pogg. Ann.*, **113**, 513 (1861) first qualitatively explained electrokinetic phenomena on the basis of the existence of an electric double layer. It should be remembered that the ideas of Quincke and Helmholtz appeared before the Arrhenius dissociation theory.

tend to move in opposite directions when the current flows through the cell. We can calculate the velocity of the solid with reference to that of the liquid by assuming that the liquid is stationary. This is electrophoresis. We can calculate the velocity of the liquid with reference to that of the solid by assuming that the solid is stationary. This is electrosmosis. It is immaterial whether we choose to calculate the velocity of the solid or of the liquid; we obviously obtain exactly the same equation for both.

The electric force per unit of solid surface is $X\sigma$ where X is the applied electric field strength and σ is the number of charges per unit of surface. When the particle has attained a constant velocity, the electrical force of acceleration must be equal to the retarding force of friction,

$$\eta\frac{\bar{v}}{r}, \tag{1}$$

where $\bar{v}$ is the velocity of the solid particle, r the thickness of the double layer, and η the viscosity of the pure solvent. It is assumed that the double layer is contained entirely in the liquid, that the layer of liquid next to the solid is held firmly to the solid and that the velocity gradient between the moving particle and the pure solvent is contained entirely within the thickness of the double layer r.* Equation (1) results simply from the fact that the force of friction is proportional to the viscosity, to the surface causing friction (here taken as unit surface) and to the velocity gradient $\bar{v}/r$. When the velocity becomes constant,

$$X\sigma = \eta\frac{\bar{v}}{r}. \tag{2}$$

The double layer may be treated as a condenser of charge density σ, potential ζ, dielectric constant D, and thickness r. From the equations of a condenser, (4) and (7) of Chap. XI, we have

$$\frac{\sigma}{\zeta} = \frac{D}{4\pi r} \tag{3}$$

* For a more extensive mathematical and thermodynamic treatment of electrokinetic and electrocapillary phenomena see F. O. Koenig, "Handbuch der Experimentalphysik," Vol. 12, Part 2, Chaps. 5 and 6, Leipzig, 1933; and H. A. Abramson, "Electrokinetic Phenomena and Their Application to Biology and Medicine," Chemical Catalog Company, Inc., New York, 1934.

Eliminating σ and r from Eqs. (2) and (3), we obtain for the velocity of the colloidal particle

$$\bar{v} = \frac{\zeta X D}{4\pi\eta}. \tag{4}$$

The velocity of the colloidal particle is therefore proportional to the potential of the double layer, the applied e.m.f. and the dielectric constant of the dispersion medium and inversely proportional to the viscosity. Equation (4) also predicts that the velocity of the particle is independent of the size and shape and bulk conductance of the particle. Debye and Hückel,* however, conclude that the factor $1/4\pi$ of Eq. (4) is valid only for cylindrical particles whereas the factor $1/6\pi$ should be substituted in the case of spherical particles. Henry† has extended the mathematical analysis further with the conclusion that the factor $1/4\pi$ applies only to cylindrical particles placed axially to the applied field whereas the factor $1/8\pi$ should be introduced in the case of cylindrical particles placed broadside to the field. Abramson and Michaelis‡ investigated the influence of size and shape upon electrophoretic mobility. They observed the velocity of long, narrow asbestos needles and of spherical droplets of various oils such as Nujol, benzyl alcohol, castor oil, etc. They covered these different particles with a film of protein material so that the particles would have surfaces of the same chemical composition. Abramson and Michaelis found that the velocity of migration is "determined solely by the surface characteristics of the particle and is independent of both size and shape within the limits studied." This is illustrated by Fig. 5. The long narrow particle is an asbestos needle and moves to the right let us say (without changing its orientation), with a relative velocity 6.4. The oil droplet moves with a relative

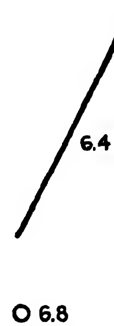


FIG. 5.—Diagram illustrating the independence of velocity on size and shape.

* P. DEBYE and E. HÜCKEL, *Physik. Z.*, **25**, 49 (1924).

† D. C. HENRY, *Proc. Roy. Soc.*, **A 133**, 106 (1931).

‡ H. A. ABRAMSON and L. MICHAELIS, *J. Gen. Physiol.*, **12**, 587 (1929). See also the discussion by ABRAMSON, "Electrokinetic Phenomena," Chap. IV, Chemical Catalog Company, Inc., New York, 1934.

velocity 6.8. The conclusions of Abramson and Michaelis are in accord, therefore, with the Helmholtz-Smoluchowski theory rather than in accord with the theory of Debye and Hückel. Mooney,* however, points out that the assumptions of the Debye and Hückel theory make their equation valid for very dilute solutions and for ultramicroscopic particles composed of only a few molecules and carrying only a few elementary charges. The Helmholtz equation, on the other hand, is valid for any particle suspended in an aqueous solution provided the radius of curvature is large in comparison with the thickness of the double layer (provided his other assumptions are also justified).

Equation (4) may also be tested by determining the velocity of the colloidal particle as the viscosity is changed. If we assume that D and ζ are independent of the temperature, $\eta\bar{v}$ should be constant at different temperatures. Burton† has carried out some experiments on the electrophoresis of colloidal aqueous silver solutions which prove that $\eta\bar{v}$ is constant. His data are given in Table I. McTaggart also verified Eq. (4) in his gas bubble experiments by proving that the velocity of motion was proportional to the potential gradient and was independent of the size of the bubble.

TABLE I.—INFLUENCE OF TEMPERATURE ON ELECTROPHORESIS

t, °C.	$\bar{v}$, cm./sec. for 1 v./cm.	η	$\eta\bar{v}$
11°	1.96×10^{-4}	0.01282	2.51×10^{-6}
21°	2.52×10^{-4}	0.00992	2.52×10^{-6}

If we accept Eq. (4) as correct, it is possible to calculate the potential of the double layer, ζ, from the velocity measurements. Table II contains some characteristic data taken from Freundlich's‡ "Colloid and Capillary Chemistry."

It is interesting to note that despite great differences in size and in chemical constitution of the dispersed phase, the colloidal particles all have about the same velocity and that the magnitude

* MELVIN MOONEY, *J. Phys. Chem.*, **35**, 331 (1931).

† BURTON, *Phil. Mag.*, (6), **11**, 440 (1906).

‡ H. FREUNDLICH "Colloid and Capillary Chemistry," p. 257, transl. by H. S. Hatfield, E. P. Dutton & Co., New York.

of the velocity is nearly identical with that of ions in aqueous solution. Practically all of the colloidal particles including oil drops and air bubbles have a negative ζ-potential and migrate, therefore, toward the positive electrode. Basic colloids such as oxides, hydroxides and carbonates of the metals have positive ζ-potentials, however. The two values of gold and platinum given in Table II were obtained by different investigators. The discrepancies are probably due to differences in purity of the colloidal solution. As we shall immediately see, the electrophoretic velocities are extraordinarily sensitive to slight changes in the chemical nature of the dispersion medium.

TABLE II.—ζ-POTENTIALS FOR COLLOID PARTICLES DISPERSED IN PURE WATER

Dispersed phase	Diameter of particle	$\bar{v}$, cm./sec. per 1 v./cm.	ζ, volts
As_2S_3	Below 50$\mu\mu$	2.2×10^{-4}	−0.032
Quartz	1μ	3.0×10^{-4}	−0.044
Prussian blue	Below 100$\mu\mu$	4.0×10^{-4}	−0.058
Gold	Below 100$\mu\mu$	4.0×10^{-4}	−0.058
Gold	Below 100$\mu\mu$	2.2×10^{-4}	−0.032
Platinum	Below 100$\mu\mu$	3.0×10^{-4}	−0.044
Platinum	Below 100$\mu\mu$	2.0×10^{-4}	−0.030
Ferric oxide	Below 100$\mu\mu$	3.0×10^{-4}	+0.044
Silver	Below 100$\mu\mu$	2.4×10^{-4}	−0.034
Bismuth	Below 100$\mu\mu$	1.1×10^{-4}	+0.016
Lead	Below 100$\mu\mu$	1.2×10^{-4}	+0.018
Iron	Below 100$\mu\mu$	1.9×10^{-4}	+0.028
Oil (emulsion)	About 2μ	3.2×10^{-4}	−0.046
Air bubbles	About 0.1*mm.*	$4. \times 10^{-4}$	−0.058

The effect of dissolved ions upon the velocity and ζ-potential is complicated and little understood at the present time. However, the experimental data are interesting and definite enough so that certain generalities may be drawn. If the colloidal particle is charged negatively, as is most often the case, addition of a salt containing a univalent positive ion causes the ζ-potential to become more negative until a minimum is reached. Further increase in concentration of the salt diminishes the absolute value of the ζ-potential toward zero. This minimum of the ζ, *c* curve is

clearly shown in Fig. 6 where some data obtained by Powis* on oil drops in water are plotted. Both potassium chloride and potassium ferrocyanide produce minima in the curves, but the minimum disappears if salts containing positive ions with valences greater than unity are added to the solution. In the case of thorium chloride, having a positive ion valence of 4, the ζ-potential is made positive to such an extent that in the most

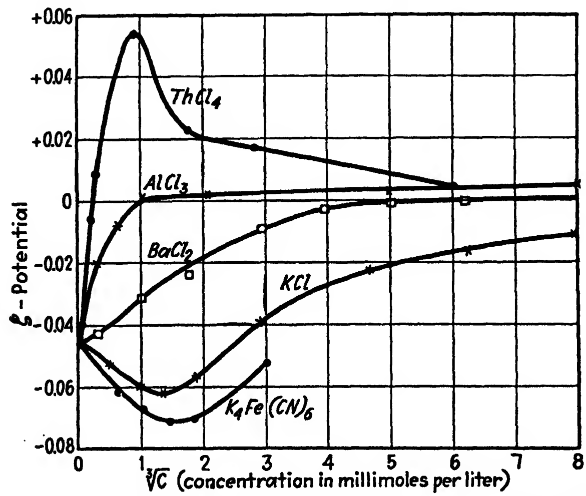


FIG. 6.—Data of Powis illustrating effect of electrolyte concentration upon electrophoretic mobility of oil drops in water.

dilute range a maximum in the ζ-potential occurs. Of course, a change in the sign of the ζ-potential implies a reversal in the direction of migration of the colloidal particle. Freundlich†

TABLE III.—INFLUENCE OF $Th(NO_3)_4$ UPON THE ELECTROPHORETIC MOBILITY OF AIR BUBBLES

Electrolyte Concn., Micromoles per Liter	Relative Velocity of Air Bubble
0.017	−0.040
0.17	+0.013
1.7	+0.018
3.5	+0.021
7.0	+0.025

* POWIS, *Z. physik. Chem.*, **89**, 91 (1915).

† FREUNDLICH, "Colloid and Capillary Chemistry," p. 279, E. P. Dutton & Co., New York.

recalculates some of McTaggart's air bubble data to illustrate the pronounced effect of thorium ions (see Table III). The addition of only one tenth of a milligram of thorium nitrate per liter of solution is sufficient to change the direction of motion of the air bubble. It should be noted that at relatively high concentrations of any electrolyte the ζ-potential approaches zero. This means that electrophoresis is only appreciable in very dilute solutions.

When the ζ-potential is zero, the electrophoretic velocity is zero, and the colloid is at its *isoelectric point*. The attainment of the isoelectric point is important for the coagulation of colloids, since hydrophobe sols* are unstable and may precipitate when their surface charge is neutralized; that is, when the colloid is at the isoelectric point.

Positive colloids have not been studied to the same extent as negative colloids, yet from the results obtained with colloidal particles having a negative ζ-potential, we might predict that negative ions have a greater effect on positive colloids than do positive ions. Burton† has determined the concentration of some electrolytes necessary to lower the electrophoretic velocity of positive copper oxide colloidal particles by 20 per cent. His results, given in Table IV, show that negative ions of a high valence cause a marked lowering of the ζ-potential.

TABLE IV.—EFFECT OF ANIONS OF DIFFERENT VALENCES UPON THE ELECTROPHORETIC VELOCITY OF POSITIVE COPPER OXIDE PARTICLES

Temperature = 18°C.

Electrolyte	Concentration (Millimoles per Liter) Necessary to Reduce Velocity 20%
KCl	115
K_2SO_4	49
$K_3Fe(CN)_6$	2.2

Migration or Sedimentation E.M.F.—It is reasonable to expect that if an applied e.m.f. can cause electrophoresis, the motion of a colloidal particle in the absence of the applied e.m.f. will produce an e.m.f. Not much work has been done on this subject, however, due to the difficulty in obtaining exact results.

* Hydrophobe sols are formed from substances not easily wetted by water.
† BURTON, *Phil. Mag.*, (6), **17**, 583 (1909).

The existence of e.m.fs. produced by falling colloidal particles was first discovered by Dorn* and is called the Dorn effect. One of the most recent investigations is that of Burton and Currie.†

Procopiu‡ has recently measured the e.m.f. developed between similar electrodes in the same solution when one of the electrodes is shaken. The observed e.m.f. is not strictly an electrokinetic potential but bears a strong resemblance to it; *i.e.*, the change in e.m.f. on shaking is affected by ions in much the same way that the ζ-potential is. It also bears the same sign.

Electrosmosis.—Electrosmosis is the reverse of electrophoresis; it is the migration of the dispersion medium if the dispersed phase is held stationary. In this case we must consider the wall of a capillary tube or the walls of capillaries inside membranes as being the dispersed phase. The liquid adhering to the solid wall is charged, according to the concept of the Helmholtz double layer, with electricity of one sign, and the adjoining layer of movable liquid is charged with electricity of the opposite sign. On applying an external e.m.f. the oppositely charged layers of liquid will be attracted to opposite poles of the cell, and if the solid wall of the capillary is held stationary, the liquid will move in the capillary. The velocity of motion is exactly the same as the electrophoretic velocity and is given by the same equation

$$\bar{v} = \zeta\frac{XD}{4\pi\eta}. \tag{4}$$

The experimental method of von Elissafoff§ for the measurement of electrosmosis consisted in determining the rate of efflux of liquid from a narrow capillary placed horizontally between two electrodes. A small air gap separated both electrodes from the liquid, thereby giving to the cell a very great electrical resistance. The advantage of this method over the customary procedure of using a diaphragm is that the glass capillary can be more readily rinsed and cleaned than can a diaphragm. The

* Dorn, *Wied. Ann.*, **10**, 70 (1880).

† Burton and Currie, *Phil. Mag.*, (6), **49**, 194 (1925); See also Bull, "Colloid Symposium Annual," Vol. VII, p. 115, John Wiley & Sons, Inc., New York, 1930.

‡ S. Procopiu, *Z. physik. Chem.*, **154 A**, 322 (1931).

§ Von Elissafoff, *Z. physik. Chem.*, **79**, 385 (1912).

disadvantage is that the large electrical resistance made necessary the use of a static machine for the production of a high e.m.f. The electrical conditions were, therefore, not well defined.

Since the same law governs the velocity of electrosmosis, it is not surprising that electrosmosis is influenced by the electrolyte concentration of the solution in much the same way that electrophoresis is affected. The effect of thorium nitrate upon the electrosmosis of water in quartz capillaries was determined by von Elissafoff with the results given in Table V where V is the volume of flow in unit time.

TABLE V.—INFLUENCE OF $Th(NO_3)_4$ UPON THE ELECTROSMOSIS OF WATER IN QUARTZ CAPILLARIES

Concn. of $Th(NO_3)_4$ (Micromoles per Liter)	V
0	−50
0.36	−27
1.0	−2
1.9	0
3.8	+12

Basic dyes such as new fuchsin and crystal violet are very active and reverse the charge of capillaries at low concentrations, although not at such low concentrations as thorium nitrate solutions.

Interesting results may be obtained if the electrosmosis measurements are carried out in an apparatus which permits the electrosmotic flow to take place vertically rather than horizontally. When the current is passed through the cell, the dispersion medium will be transported and will rise in its vertical tube until the increased pressure is just sufficient to balance the electrosmotic force. The relation between the height of liquid and the applied e.m.f. may be derived in the following way. The volume of liquid, V, which flows through the capillary tube in unit time is given by the equation

$$\pi r^2 \bar{v} = V. \tag{5}$$

Eliminating $\bar{v}$ from Eq. (5) by means of Eq. (4), we obtain

$$\bar{v} = \frac{\zeta X D}{4\pi\eta} = \frac{V}{\pi r^2}$$

or

$$V = \frac{\zeta r^2 X D}{4\eta}. \tag{6}$$

For X, the field strength, we may substitute E/l, where E is the applied e.m.f. and l is the distance between the electrodes in the cell:

$$V = \frac{\zeta r^2 E D}{4\eta l}. \tag{7}$$

Poiseuille's law for viscous flow is

$$V = \frac{\pi P r^4}{8\eta l}, \tag{8}$$

where P is the hydrostatic pressure, r is the radius of the capillary tube, and l is the length of the capillary. Eliminating the volume from Eqs. (7) and (8) gives us the desired relationship

$$V = \frac{\pi P r^4}{8\eta l} = \frac{\zeta r^2 E D}{4\eta l}$$

or

$$P = \frac{2\zeta E D}{\pi r^2}. \tag{9}$$

Hence at equilibrium the height to which a column of liquid rises in a capillary tube, for any given tube, is directly proportional to the applied e.m.f., to the ζ-potential and to the dielectric constant of the liquid. Coehn and Raydt* measured the electrosmotic rise for a considerable number of organic liquids and discovered the interesting rule that the heights of rise, h (which in their apparatus were directly proportional to the pressure), are proportional to the differences between the dielectric constants of the liquid and that of glass, or

$$\frac{h}{h_0} = \frac{D - D_G}{D_0 - D_G}. \tag{10}$$

D and h are the dielectric constant and height of rise for one liquid, D_0 and h_0 similar quantities for acetone, the reference liquid, and D_G is the dielectric constant of glass. Table VI gives some data for the dielectric constant of a number of liquids obtained by Coehn and Raydt from their electrosmotic measurements.

* Coehn and Raydt, *Ann. Physik*, (4) **30**, 777 (1909).

TABLE VI.—DIELECTRIC CONSTANT DATA OBTAINED FROM ELECTROSMOTIC MEASUREMENTS

Liquid	h	D	D (from capacity measurements)
Water	+210	81	81
Nitrobenzene	+ 88.5	37.6	37.2
Acetonitrile	+106	43.6	36.4
Methyl alcohol	+ 80	34.5	34
Nitrotoluene	+ 51	24.2	27
Acetone	+ 60	27.5	26.5
Ethyl alcohol	+ 58	26.6	25.5
Isobutyl alcohol	+ 29.5	16.5	18.75
Benzaldehyde	+ 19	12.8	14
Pyridine	+ 14.4	11.3	12.4
Aniline	+ 7.8	8.8	7.3
Chloroform	− 1.67	5.4	5.18
Ethylene bromide	− 2.95	4.95	4.87
Benzene	− 8.9	2.8	2.4

A study of Table VI shows that electrokinetic phenomena are particularly marked in liquids of high dielectric constant.

Streaming E.M.F.—If an applied e.m.f. produces an electrosmotic flow of liquid in a capillary tube, it is reasonable to expect that the motion of a liquid in a tube due to mechanical forces will produce a detectable e.m.f.. This is indeed found to be the case; the observed voltages are called streaming e.m.f. due to the fact that they arise when a liquid streams through a capillary tube.

Bull and Gortner* have recently made an extensive study of the streaming e.m.f. Their cell, designed by Martin and Gortner,† is illustrated in Fig. 7. The liquid under investigation was forced through the perforated gold electrodes and the diaphragm. The diaphragm was made out of cellulose (filter paper pulp), and after shaking with the liquid, the cellulose was packed tightly into place. Compressed air was the source of pressure; the pressure was measured by means of a water manom-

* H. B. BULL and R. A. GORTNER, *J. Phys. Chem.*, **35**, 309, 456, 700 (1931); *Proc. Nat. Acad. Sci.*, **17**, 288 (1931).

† W. M. MARTIN and R. A. GORTNER, *J. Phys. Chem.*, **34**, 1509 (1930).

eter immediately after the e.m.f. between the gold electrodes had been determined by the electrometer-potentiometer circuit.

For any given diaphragm and liquid the measured e.m.f. should be directly proportional to the pressure according to Eq. (9).

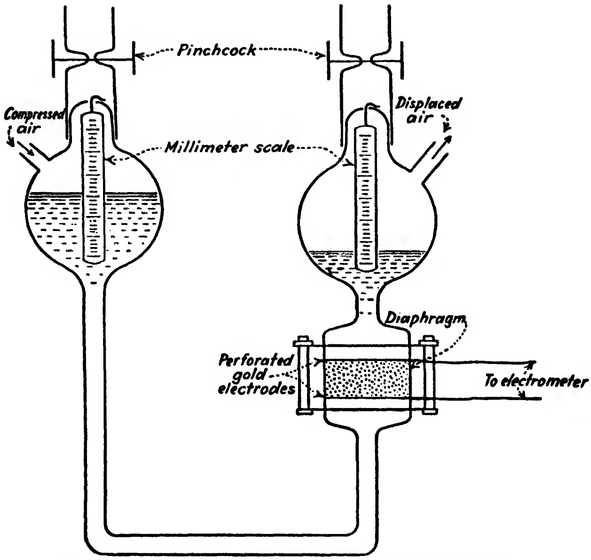


FIG. 7.—Cell for the measurement of streaming e.m.f.

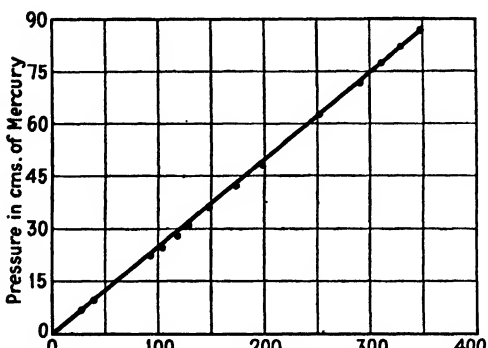


FIG. 8.—The relation between streaming e.m.f. and pressure.

Bull and Gortner tested this prediction and obtained the results shown in Fig. 8. The data amply verify the predicted proportionality between the e.m.f. and the pressure.

Freundlich and Rona* made use of a single capillary tube instead of a porous plug to measure the streaming e.m.f. Figure 9 illustrates their apparatus; the capillary tube K is easily removed and changed by means of ground joints. Reversible calomel electrodes, E and E', were used to make contact between the liquid under investigation and the electrometer circuit. The

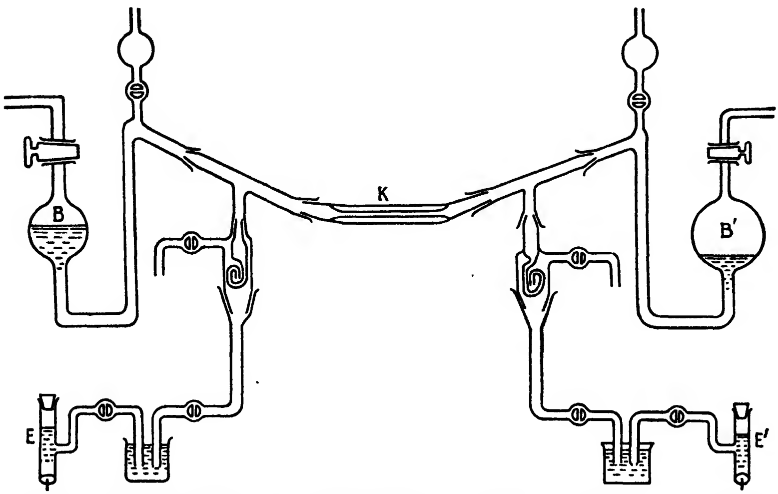


FIG. 9.—Freundlich and Rona's apparatus for streaming-e.m.f. measurements.

liquid was driven in a strong stream through the capillary tube by the pressure from a gas cylinder, and the e.m.f. developed between the two calomel electrodes was measured.

According to the Helmholtz theory the equation for the streaming e.m.f. E is

$$E = \frac{P\zeta D}{4\pi\eta\kappa}, \tag{11}$$

where κ is the specific conductance of the liquid.

The results of measurements of the streaming e.m.f. are similar to data obtained in other electrokinetic measurements. Bull and Gortner found that thorium chloride was able to reverse the sign of the ζ-potential on cellulose-water boundaries. Freundlich and Rona obtained similar results with glass-water boundaries.

* FREUNDLICH and RONA, *Sitzungsber. Preuss. Akad. Wiss.*, **20**, 397 (1920).

Bull and Gortner also point out that ζ-potential-concentration curves for oil-aqueous solution, glass-aqueous solution, and cellulose-aqueous solution, closely resemble each other. In general we may conclude that whatever the method of measuring the ζ-potential the ζ-potential-concentration curves for aqueous solutions against a negatively charged wall will have the general shape of the curves in Fig. 10.

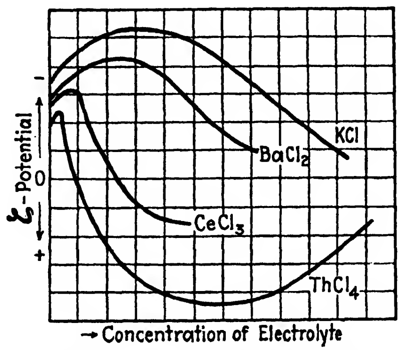


FIG. 10.—General form of the ζ-potential-concentration curve.

Significance of the ζ-Potential.—If the ζ-potential is the interfacial potential existing at a metal-solution boundary, and if it has the properties given to it by Helmholtz, one could expect that the ζ-potential and the thermodynamic potential measured in a galvanic cell, which we shall call the Nernst potential and shall designate by the symbol E, would be identical. This is the idea which prompted Billitzer* in 1902 to attempt a measurement of the absolute zero of potential. Billitzer believed that when he had brought the electrophoretic mobility of a metal colloid to zero by changing the metal ion concentration in the solution, the ζ-potential would be zero and *also the Nernst potential would be zero.* Thus, if the colloid particle in a particular solution does not move under an applied e.m.f., the potential of the metal-solution boundary as measured in a galvanic cell should be zero. Billitzer in this way determined the absolute zero of potential, but his value differed by more than half a volt from that obtained in electrocapillary measurements (described below); a fact which immediately led one to suspect that ζ and E were not identical. The lack of any relationship between the ζ-potential and the

* BILLITZER, *Z. Elektrochem.*, **8**, 638 (1902).

Nernst potential was definitely proved by the classic experiments of Freundlich and Rona.* These authors measured ζ and E for identical phase boundaries, and found no connection between the two. By means of the Haber glass electrode (see Chap. XXV) they measured the Nernst potential E. The Nernst potential might be called the perpendicular potential since the electric current flows perpendicularly to the surface of the glass during the measurement. Using the same glass and the same solution Freundlich and Rona next measured by the streaming-e.m.f. method the ζ-potential. The ζ-potential is sometimes called the tangential potential because the electric current flows tangentially to the glass surface during the measurement of E from which ζ is calculated by means of Eq. (11). The ζ-potential was very strongly affected by minute quantities of ions of high valence as already mentioned, but the glass electrode potential depended only upon the hydrogen ion concentration of the solution and not at all upon the presence of other ions (except in so far as the hydrogen ion activity coefficient was altered). The ζ-potential is, therefore, not equal to the total potential across the phase boundary.

To explain this discrepancy we must make use of the concept of the diffuse double layer as developed by Stern.†

Up to this point we have assumed that the double layer consists of first a layer of charges in a film of liquid rigidly attached by surface forces to a solid wall and second, a movable layer of charges on the liquid side of the double layer. We have assumed that these charges are contained in layers having the thickness of an atomic diameter. Both of these assumptions are probably incorrect and in fact to a certain extent unnecessary. The diffuse double layer theory states that the layer of charges on the liquid side of the double layer has a thickness considerably

* Freundlich and Rona, *Sitzungsber. Preuss. Akad. Wiss.*, **20**, 397 (1920); Freundlich and Ettisch, *Z. physik. Chem.*, **116**, 401 (1925); see also G. W. Smith and L. H. Ryerson, *J. Phys. Chem.*, **38**, 133 (1934) (ζ-potentials of thin metal films).

† O. Stern, *Z. Elektrochem.*, **30**, 508 (1924). Stern's theory represents a synthesis of older ideas of Helmholtz, Gouy, Chapman and Herzfeld: G. Gouy. *Compt. Rend.*, **149**, 645 (1909); *Ann. de physique*, (9) **7**, 129 (1917); D. L. Chapman, *Phil. Mag.*, **25**, 475 (1913); K. F. Herzfeld, *Phys. Z.*, **21**, 28 (1920).

greater than an atomic diameter and that this layer may not all be free to move. The thickness of the double layer is to be pictured in the same way as the thickness of the ionic atmosphere in the modern theory of electrolytes; with increase of concentration the thickness of the double layer decreases. In pure water Gouy calculates that the double layer has a thickness equal to 1×10^{-4} cm. and in a 0.1 N solution 1×10^{-7} cm. A schematic representation of the diffuse double layer is given in Fig. 11 where the solid horizontal line divides the layer of positive fixed charges from the diffuse layer of negative and positive charges which is partly fixed and partly movable. Because of the necessity of electroneutrality of the colloidal solution the sum of the positive charges above the solid line must equal the sum of the excess

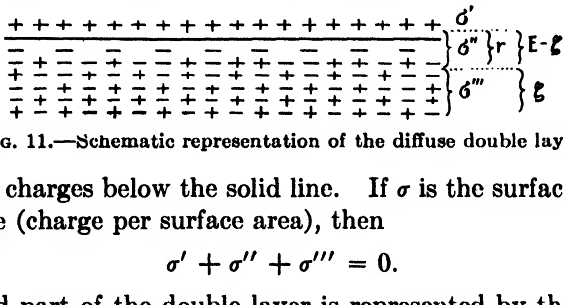


FIG. 11.—Schematic representation of the diffuse double layer.

negative charges below the solid line. If σ is the surface density of charge (charge per surface area), then

$$\sigma' + \sigma'' + \sigma''' = 0.$$

The fixed part of the double layer is represented by the charges $\sigma' + \sigma''$, while the charges of the movable part of the double layer are represented by the symbol σ'''. Stern assumes that only electrostatic and thermal forces act on the charges in the movable part of the double layer, but that specific adsorption forces in addition to the electrostatic and thermal forces have to be considered in connection with the fixed part of the double layer.

Since the double layer extends into the liquid, the interfacial potential will not fall abruptly but will change at first rapidly and then more slowly so that part of the difference of potential will be found entirely in the movable part of the double layer. The total drop of potential across the whole double layer is equal, presumably, to the Nernst potential while the drop of potential in the movable part of the double layer is equal to the ζ-potential. Stern assumes that the potential varies linearly along a line vertical to the solid wall within the rigid part of the double layer; in

the movable part of the double layer, however, the potential falls off gradually to the value it has in the recesses of the liquid phase. The variation of potential with distance is shown schematically in Fig. 12 where ordinates represent potentials and abscissas distance from some arbitrary point within the solid. In Fig. 12*a* both E and ζ are positive, while in Fig. 12*b* E is positive and ζ negative. In the measurement of e.m.f. in a galvanic cell, the entire potential drop E is measured since the current flows vertically or transversely to the surface. In electrokinetic measurements, however, the potential calculated from the measurements, the ζ-potential, is only that between the layer of firmly held liquid and the movable liquid.

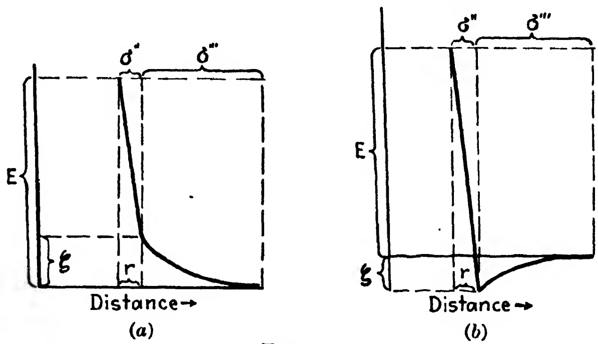


FIG. 12.

Although we do not know exactly how the interfacial potential is set up (see the next chapter for the mathematical theory of the double layer), *i.e.*, we do not know what forces produce interfacial potentials represented by the two curves of Fig. 12, nevertheless qualitative consideration of the curves enables us to gain ideas concerning the influence of adsorption on the ζ-potential. Thus, the ability of thorium ions to reverse the sign of the ζ-potential without changing the magnitude of the Nernst potential may be explained by assuming that the thorium ions are adsorbed in the movable liquid layer causing the potential at this point to become more positive. If the ζ-potential was originally negative, the potential-distance curve might have the shape of Fig. 12*b*; adsorption of thorium ions would change the shape of the curve to that of Fig. 12*a* without changing the value of the Nernst potential. While adsorption will in this way have an

overwhelming influence on the ζ-potential and electrokinetic processes in general, adsorption will have little if any influence upon the total potential change, the Nernst potential. By studying Fig. 12 we can readily see also that the ζ-potential may become equal to zero without the Nernst potential becoming equal to zero. Hence, we cannot hope to realize the absolute zero of potential from electrokinetic measurements.

Biological and Industrial Significance of Electrokinetic Phenomena.—Electrophoresis and electrosmosis undoubtedly occur continually in the human body. Abramson* has recently discussed the biological significance of the electrophoresis of blood cells, and he points out that the migration of the polymorphonuclear leucocyte through the gel-like structure of the blood capillary to a point of injury is probably an electrophoretic migration produced by a difference in e.m.f. between injured and uninjured tissues. Although we know that e.m.fs. are produced and exist in the human body, we do not know much about them as yet.

Perhaps the largest scale industrial application of electrophoresis is the Cottrell process for the removal of mist or smoke in smelter flues and in other factory smoke stacks. This process is based upon the fact that if a needle point is connected to one side of a high-voltage direct-current line and a flat plate to the other side, the air between the two becomes charged with electricity and any objects, even gas molecules, that are suspended in the air become likewise charged with electricity and move toward the flat plate. Cottrell† believed that this principle could be applied to the removal of suspended bodies in flue gases which had never, hitherto, been completely freed of dust particles. The method consisted in building by means of mica or asbestos fastened on wires a number of pointed electrodes in the flue, and connecting these electrodes to the high potential direct current source. The dust particles pick up an electric charge and migrate to the walls of the flue where the charge is neutralized and the particles settle out. Cottrell's method is very successful

* H. A. Abramson, "Colloid Symposium Monograph," Vol. VI, p. 115 New York, (1928); "Electrokinetic Phenomena and their Application to Biology and Medicine," Chemical Catalog Company, Inc., New York, 1934.

† Cottrell, *J. Ind. Eng. Chem.*, **3**, 542 (1911).

commercially; in one plant, the Washoe reduction works of the Anaconda Copper Mining Company, there are 111 miles of chains covered with point electrodes in use.

Electrophoresis is used in the precipitation of rubber from latex; the solid layer of rubber forms at the anode when a direct current is passed through latex. This process has been used extensively in Java. Sulfur, fillers, pigments, and softeners may be suspended in the latex and the resulting mixture electrolyzed so that the compounds in the mixed solution deposit uniformly and in substantially the same proportion as in the solution. Rubber with materials necessary for vulcanization can be precipitated electrically upon fabric or other porous materials.*

The attempt has been made to remove a part of the 90 per cent of water that is found in peat by subjecting the peat to an external electric field. The peat migrates to the anode where it deposits as a solid containing 50 to 60 per cent water. The subsequent drying of the peat proved to be too costly for the process to be a commercial success.

Electrosmotic processes have been applied to the dewatering and purification of clay, in electrical tanning of leather, and in electrical "lubrication" of the wires used in cutting clay bricks. A long list of patents concerning technical applications of electrophoresis and electrosmosis have been compiled by Prausnitz and Reitstötter.†

Exercises

1. The velocity of a colloidal particle in water at 18°C. is 0.0035 mm. per second in the direction of the positive electrode when the voltage applied to the two end-electrodes 8 cm. apart is 5 v. Calculate the ζ-potential of the particle in volts (one e.s.u. = 300 v.).

2. Predict the velocity of the colloidal particle of Exercise 1 if the solution is made 5×10^{-6} molal in thorium nitrate.

3. From the data of Table III calculate the concentration of thorium nitrate necessary to bring the colloidal air bubble to its isoelectric point.

4. Prove that Eq. (4) is dimensionally correct.

* Sheppard and Eberlin, U.S. Patent No. 1,476,374 (1923).

† Prausnitz and Reitstötter, "Elektrophorese, Elektroosmose and Elektrodialyse," Verlag von Theodor Steinkopff, Dresden, 1931, see also C. L. Mantell, "Industrial Electrochemistry," Chap. IX, McGraw-Hill Book Company, Inc., New York, 1931. For an application to mineral flotation see Bull, Ellefson, and Taylor, *J. Phys. Chem.*, **38**, 401 (1934).

CHAPTER XXVII

ELECTROCAPILLARY PHENOMENA

The relations between interfacial potential and surface tension and adsorption are very interesting. There are two general methods for studying these relations, one is to measure the surface tension as the electric potential difference at the interface is varied and the second method is to measure the change in interfacial potential as the interfacial surface is altered by allowing various substances to be adsorbed at the interface.

The Capillary Electrometer.—In 1873 Lippmann* developed an apparatus, called the capillary electrometer, by means of which the interfacial tension of mercury against an aqueous solution can be measured as the potential between the mercury and the aqueous solution is altered. His apparatus is illustrated in Fig. 1., where C is a small cone-shaped capillary tube 10 to 50 microns in diameter, A is the aqueous solution into which dip the capillary tube C and a salt bridge to the electrode C'. The upward force of the interfacial tension at C is sufficient to support a column of mercury K whose height is easily varied by means of the leveling bulb. As the interfacial tension increases a greater column of mercury can be supported; the exact relationship between height h and interfacial tension γ is given by the usual surface tension equation

$$\gamma = \frac{hdgr}{2}, \tag{1}$$

where d is the density of mercury, g the acceleration due to gravity, and r the radius of the capillary tube. Equation (1) tells us that for any definite temperature and apparatus the interfacial tension is directly proportional to the height. In actual practice the meniscus of the mercury in the small capillary is held constant, and the height of the mercury column is varied by raising or lowering the mercury leveling bulb.

* G. Lippmann, *Pogg. Ann.*, **149**, 547 (1873).

The electrode C' (Fig. 1) may be a reversible electrode such as a calomel electrode, or some other nonpolarizable electrode such as a large flat mercury surface. Lippmann discovered that when an external voltage was applied at P_1 and P_2 making the mercury at C the cathode, *i.e.*, the applied e.m.f. caused positive electricity to flow from the aqueous solution toward the mercury capillary surface, the interfacial tension of the mercury was increased so that a longer column of mercury could be supported in K. It is not practical to make C the anode due to the fact that the

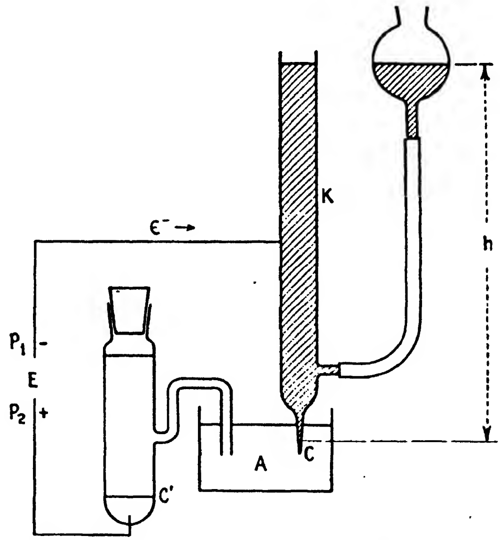


FIG. 1.—Schematic representation of the capillary electrometer.

mercury oxidizes readily, thus preventing the measurement of the interfacial tension.*

If the applied voltage E is increased so that more electrons accumulate (supposedly) on the mercury side of the mercury-aqueous solution interface, the interfacial tension is further increased, but eventually a value of E will be reached at which an increase of E decreases the interfacial tension rather than increases it. If the interfacial tension γ or the height h is plotted as a function of the e.m.f., the so-called electrocapillary curve is obtained. Such a curve is illustrated in Fig. 2 which represents the inter-

* For experimental details see F. O. Koenig, *Z. physik. Chem.*, **154 A**, 454 (1931).

facial tension of mercury as a function of the applied voltage in a solution one normal in potassium nitrate and about 0.001 N in

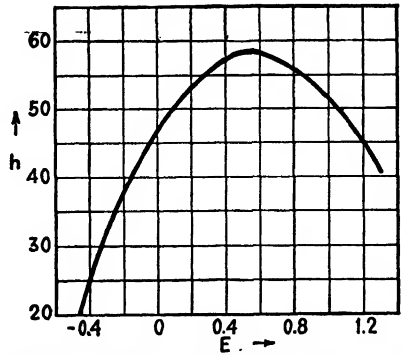


FIG. 2.—Electrocapillary curve for mercury in 1-N potassium nitrate solution.

Hg_2^{++} ions.* The voltage values are those for a normal calomel electrode acting as the auxiliary electrode (the anode).

In order to obtain an electrocapillary curve free from error, the mercury electrode C must be made the negative electrode, the concentration of Hg_2^{++} ions in the aqueous solution (at A) must be small in comparison with the total electrolyte concentration, and the concentration of the ions taking part in the electrode reaction at C' must be greater than 10^{-4}, as Koenig points out. Koenig also found that substitution of a quartz capillary for a glass capillary did not change the results. The capillary electrometer may be used as a null point instrument in place of a galvanometer in e.m.f. measurements, although it is not so sensitive. When the capillary electrometer is thus used, the apparatus takes the form illustrated in Fig. 3. Application of an e.m.f. causes the mercury meniscus to move in the narrow

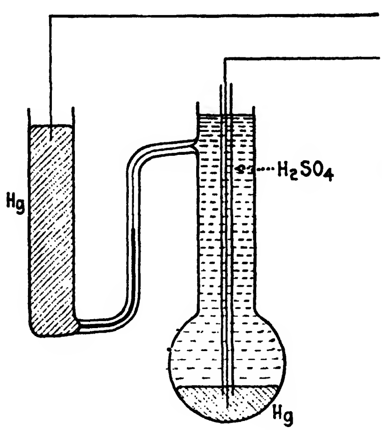


FIG. 3.—Lippmann capillary electrometer.

* F. O. KOENIG, *Z. physik. Chem.*, A 154, 464 (1931).

capillary tube. By observing the meniscus with a microscope, it is possible to balance the unknown e.m.f. with the potentiometer until the meniscus does not move when the key is tapped.

Influence of Dissolved Substances on the Electrocapillary Curve.—The shape of the electrocapillary curve in Fig. 2 may be considerably altered by the presence of certain ions in the solution.* Thus, the position of the maximum of the electrocapillary curve is shifted toward higher values of E (mercury side of the interface more negative) by the presence of salts containing sulfide, iodide, and thiocyanate ions. Figure 4, taken from Frumkin's paper, contains a number of electrocapillary curves for mercury in potassium salt solutions. Positive ions usually do not influence the position of the maximum.

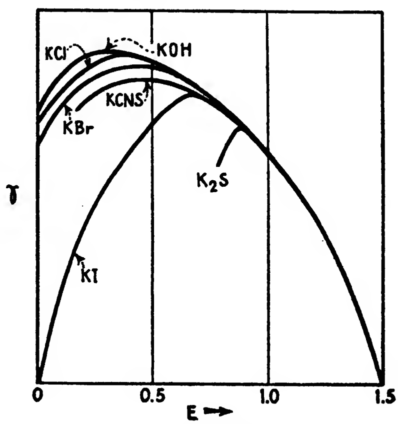


FIG. 4.—Electrocapillary curves for mercury in solutions of different inorganic electrolytes.

Organic compounds may shift the maximum of the curve to higher or lower values of E, or they may not shift the maximum at all. In general aliphatic oxygen compounds with one polar group such as the alcohols, acids, ethers, esters, ketones, shift the maximum to lower values of E; that is, to the left in Fig. 2, while aromatic compounds such as phenol, cresol, resorcinol, nitrobenzene, etc., shift the maximum of the electrocapillary curve to higher values of E.

Not only do the dissolved substances change $E_{max.}$ (the value of E when the interfacial tension is a maximum) but they also affect the magnitude of the surface tension at the maximum. All the organic compounds cause a lowering of the $\gamma_{max.}$ whether they increase or decrease the value of $E_{max.}$, but inorganic electrolytes may either weakly increase $\gamma_{max.}$ or more or less strongly lower it. Solutions of K_2CO_3, K_2HPO_4, K_2HAsO_4, Na_2SO_4, K_2SO_4, $MgSO_4$, $Al_2(SO_4)_3$, have practically no effect upon $E_{max.}$ and

* See A. Frumkin, "Colloid Symposium Annual," Vol. VII, p. 89, New York, 1930, for a general review.

increase $\gamma_{max.}$ slightly with increase of concentration. They are called capillary inactive electrolytes. On the other hand, solutions of iodide and sulfide ions are strongly capillary active and markedly decrease $\gamma_{max.}$ as well as increase $E_{max.}$ (see Fig. 4).

Before considering the theory of the electrocapillary curve it should be pointed out that electrocapillary curves have also been obtained for bismuth, lead, tin, cadmium, zinc, and thallium amalgams and for liquid gallium.* The electrocapillary curves for most amalgams are similar to those for mercury, but the presence of thallium in the mercury lowers $\gamma_{max.}$ and raises $E_{max.}$ at lower concentrations and at high concentrations $\gamma_{max.}$ increases again. A lowering of $\gamma_{max.}$ can be explained by assuming an adsorption of thallium metal at the mercury surface.

Thermodynamics of the Electrocapillary Curve.—The energy of an interface can change in three ways, by the performance of mechanical work, by the gain or loss of heat, and by change in interfacial concentration; mathematically expressed,

$$dU = TdS + \gamma d\Omega + \sum_1^p \bar{\mu}_i dn_i + \sum_1^r \mu_j dn_j, \tag{2}$$

where U is the energy of the boundary layer, S is its entropy, Ω its surface area, $\bar{\mu}_i$ the electrochemical potential of an ionic constituent per mole [defined by Eq. (4)], μ_j the chemical potential of a neutral constituent per mole, dn_i the change in the number of moles of an ionic constituent in the interfacial layer, and dn_j the change in the number of moles of a neutral constituent in the interfacial layer. At equilibrium $\bar{\mu}_i$ and μ_j are the same on both sides of the interface. The summations are to be taken over all ionic (p) and neutral (r) constituents of the system. [Compare Eq. (2) with Eq. (32), Chap. XV]. From Eq. (2) it is possible to derive the equation†

$$d\gamma = -\frac{S}{\Omega}dT - \sum_1^p \Gamma_i d\bar{\mu}_i - \sum_1^r \Gamma_j d\mu_j, \tag{3}$$

* See the review by FRUMKIN, *Erg. d. exakten Naturwissensch.*, **7**, 235 (1928).

† See, for example, F. O. KOENIG, "Handbuch der Experimentalphysik," Vol. 12, Part 2, Chap. 5 (1933); *J. Phys. Chem.*, **38**, 111, 339 (1934): Also CRAXFORD, GATTY, and PHILPOT, *Phil. Mag.*, **17**, 54 (1934).

where Γ is the surface concentration (moles divided by surface area). The quantity Γ_i may also be defined as the amount of the ith constituent which must be added to the solution as the interfacial surface is increased by one square centimeter in order to maintain the concentration of the ith constituent in the solution constant. The electrochemical potential is defined by the equation

$$\bar{\mu}_i = \mu_i + z_i F \psi, \tag{4}$$

where z_i is the algebraic valence of the ith ion (*i.e.*, it is taken as negative for negative ions). In order to find the difference in electric potential between the mercury and aqueous phases it is necessary to consider the variations of the electrochemical potentials in the two phases. Making use of Eq. (4) and of the relation

$$\sum_1^p \Gamma_i d\bar{\mu}_i = \sum_i^{p'} \Gamma_i' d\bar{\mu}_i' + \sum_i^{p''} \Gamma_i'' d\bar{\mu}_i'', \tag{5}$$

where the superscript (′) represents the metallic phase and the superscript (″) represents the aqueous phase, Eq. (3) becomes

$$d\gamma = -\frac{S}{\Omega}dT - \sum_1^{p'} \Gamma_i' d\mu_i' - \sum_1^{p'} z_i' F \Gamma_i' d\psi' - \sum_1^{p''} \Gamma_i'' d\mu_i'' - \sum_1^{p''} z_i'' F \Gamma_i'' d\psi'' - \sum_1^{r} \Gamma_j d\mu_j. \tag{6}$$

Let us now assume that the dividing line between the two phases is coincident with the line dividing the positive and negative charges in the Helmholtz double layer. Let us also assume that the double layer is completely polarizable, *i.e.*, that it acts like a perfect condenser (no current flows through the double layer); then we can write $d(\psi' - \psi'') = -dE$, where E is the externally applied e.m.f. If σ is charge density defined by the equation

$$\sigma = zF\Gamma, \tag{7}$$

the electroneutrality and complete polarizability of the system require that

$$\sigma' = -\sigma''. \tag{8}$$

Making use of these relations Eq. (6) becomes

$$d\gamma = -\frac{S}{\Omega}dT - \sum_1^{p'} \Gamma_i' d\mu_i' - \sum_1^{p''} \Gamma_i'' d\mu_i'' - \sum_1^{r} \Gamma_j d\mu_j + \sigma' dE, \tag{9}$$

or at constant temperature, pressure,* and composition of both phases

$$\frac{\partial \gamma}{\partial E} = \sigma', \tag{10}$$

which is known as the Lippmann-Helmholtz equation.

Equation (10) states that the rate of change of the interfacial tension with applied e.m.f. is equal to the charge density of the mercury side of the double layer; the value $\partial\gamma/\partial E$ is the slope of the electrocapillary curve. From Eq. (10) we can conclude that the charge on the mercury side of the double layer must be positive on the rising branch of the electrocapillary curve, must be zero at the maximum and must be negative on the falling branch of the curve. From an ionic point of view it is assumed that the mercury side of the double layer is charged positively when the applied voltage is zero. As the applied voltage is increased, electrons flow toward the mercury side of the double layer (from the connection P_1, Fig. 1), thereby neutralizing the positive charge and causing the interfacial tension to rise. The interfacial tension increases with decrease of surface charge since the work necessary to increase the surface is proportional to the surface tension and the work required is less when the surface is covered by like charges which repel each other. As the applied voltage is further increased, the electrons finally neutralize the positive layer completely so that the mercury side of the double layer is uncharged and the surface tension is a maximum. With further increase of voltage the mercury side of the double layer becomes negative owing to excess electrons present, and the surface tension becomes less than its maximum value. Frumkin† has tested Eq. (10) by measuring σ' by counting and weighing drops of mercury flowing out of the capillary into the solution at the same time measuring the resulting current. The electrocapillary curve for the same system was determined in order to find the value of $\partial\gamma/\partial E$. His results are tabulated in Table I. The agreement is satisfactory even in the case of such capillary active substances as potassium iodide.

* The pressure of the mercury phase does not remain constant since the height h varies as γ varies, but this difficulty can be neglected.

† A. Frumkin, *Z. physik. Chem.*, **103**, 55 (1923); see also Schofield, *Phil. Mag.*, **1**, 641 (1926).

TABLE I.—TEST OF EQ. (10)

Solution	$\partial\gamma/\partial E$, Coul./cm.^{2}	σ', Coul./cm.^{2}
2N H_2SO_4 sat. with Hg_2SO_4	39×10^{-6}	39×10^{-6}
N NaCl sat. with Hg_2Cl_2	50×10^{-6}	47×10^{-6}
N KOH sat. with HgO	21×10^{-6}	17×10^{-6}
N KNO_3 + 0.01 *N* KI sat. with Hg_2I_2	86×10^{-6}	90×10^{-6}
N KOH + $(C_2H_5)_2O$ sat. with HgO	-1.5×10^{-6}	-1.3×10^{-6}

The Theory of the Diffuse Double Layer.—The simple Helmholtz theory of the double layer is not adequate to explain all of the experimental results; in particular it predicts that the electrostatic capacity of the double layer is independent of the concentration of the aqueous solution which is in contradiction to the facts.* The Helmholtz theory assumes that the only forces which must be considered in the double layer are the pure electrostatic forces; Gouy, on the other hand, assumes that the ions lying in the liquid side of the double layer are influenced by their thermal motion as well as by electrostatic forces. This diffuse double-layer theory can be developed mathematically by following the general procedure used later by Debye and Hückel in their interionic attraction theory of electrolytes. Making use of the Maxwell-Boltzmann distribution law and the Poisson equation, the following equation for the charge density of the diffuse double layer results:

$$\sigma''' = -\sqrt{\frac{DRT}{2\pi}\frac{c}{1{,}000}}\left(e^{\frac{F\Psi'}{2RT}} - e^{-\frac{F\Psi'}{2RT}}\right), \tag{12}$$

where σ''' is the charge density of the diffuse double layer and ψ' is the potential fall in the diffuse double layer (compare Fig. 12, Chap. XXVI). According to Eq. (12) the charge

* The capacity of the double layer according to the Helmholtz theory can be found in the following way: The capacity C is related to the charge density and the applied voltage by the equation

$$\sigma' = CE,$$

which in combination with Eq. (10) yields the equation

$$\gamma_{max.} - \gamma = \tfrac{1}{2}CE^2. \tag{11}$$

(C is the capacity per unit area of condenser plate.)

density is directly proportional to the square root of the concentration, but it is impossible to calculate σ''' due to a lack of knowledge of ψ'. One difficulty with this theory is that it does not consider specific adsorption at the interface, a difficulty which Stern has attempted to overcome. Stern* assumes that the ions of the layer falling in the liquid will be subject to forces of adsorption as well as to thermal and electrostatic forces. If Φ_+ and Φ_- are the "specific adsorption potentials" of the positive and negative ions, *i.e.*, the work which must be performed solely against adsorption forces to bring a mole of cations or anions from the solution into the fixed part of the double layer, and if Υ is the maximum number of dissolved ions which can find places on one square centimeter of interfacial surface, Stern's theory gives for the charge density σ'' in the fixed part of double layer lying on the liquid side of the interface,

$$\sigma'' = F \cdot \Upsilon \left(\frac{1}{2 + \frac{1{,}000}{V_0 c} e^{\frac{\Phi_+ + F\Psi'}{RT}}} - \frac{1}{2 + \frac{1{,}000}{V_0 c} e^{\frac{\Phi_- - F\Psi'}{RT}}} \right) \tag{13}$$

where V_0 is the molar volume of the solvent in *cc*. Since σ''' is proportional to the square root of c and σ'' approximately proportional to c it is evident that in very dilute solutions, the liquid half of the double layer will be chiefly in the movable diffuse layer. In concentrated solutions σ'' and σ''' will be nearly equal, but the charges in the diffuse double layer will be concentrated so near the solid wall that the capacity of the double layer will approximate the capacity of the Helmholtz double layer.

Stern's theory cannot be tested quantitatively, but it seems to give a reasonable picture of the double layer; it does not consider, however, a possible deformation of the adsorbed ions.

Despite the mathematical difficulties in obtaining a quantitative theory of the electrocapillary curve, it is possible to explain the effect of ions on the shape of the curves in a satisfactory qualitative manner. Referring to Fig. 4, it will be noticed that the presence of certain negative ions in the aqueous solution has a marked effect on the rising branch and on the maximum of the electrocapillary curve, but little if any effect on the falling

* O. Stern, *Z. Elektrochem.*, **30**, 508 (1924).

branch. Since the mercury surface is polarized negatively for E values higher than $E_{max.}$, it is reasonable to suppose that negative ions cannot be adsorbed at the interface and cannot, therefore, affect the course of the falling branch of the electrocapillary curve.

At the maximum according to Gouy the charge density of the mercury side of the fixed double layer is zero, $\sigma' = 0$, so that the displacement of $E_{max.}$ to higher values of E by the various ions must be due to adsorption of negative ions in the liquid side of the fixed double layer. In other words, there is a source of potential due to adsorbed ions in the liquid layer; the adsorption of the ions giving rise to an ionic distribution schematically illustrated by Fig. 5a. The presence of the adsorbed layer of negative ions lowers the interfacial tension and lowers the value of $\gamma_{max.}$.

When the mercury side of the double layer is positively charged (Fig. 5b), negative ions will have an even greater tend-

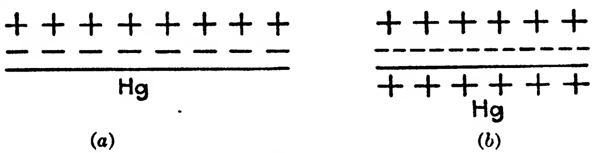


FIG. 5.

ency to be adsorbed and the rising branch of the electrocapillary curve will be markedly altered. Organic substances, electrolytes or nonelectrolytes, may affect either the rising branch of the curve or the falling branch or both; their influence is to be explained also on the basis of adsorption.

The Possibility of Determining the Absolute Zero of Potential and Single-electrode Potentials.—It was thought after the discovery of the electrocapillary curve that the capillary electrometer provided us with a method of determining the absolute zero of potential. At the maximum of the electrocapillary curve, the charge of the mercury surface is supposedly zero, a fact which led many scientists to believe that the potential difference between the mercury and the aqueous solution was also zero. If there were no charges on the mercury surface, how could a potential exist? The possibility of bringing the interfacial potential to zero in this way also suggested the possibility of

measuring single-electrode potentials by means of the following cell:

$$\text{Ag} \mid \text{AgCl} \mid \begin{array}{l}\text{NaCl}\\ \text{solution}\end{array} \mid \text{capillary electrode.}$$

If the potential between the capillary electrode and the solution is zero, the measured e.m.f. must be the potential of the single silver chloride electrode.

There are serious objections, however, to this method of measuring the absolute zero of voltage. In the first place it is not necessarily true that a zero interfacial potential must exist when the mercury surface is uncharged. The presence of substances which shift the maximum of the electrocapillary curve causes the surface tension to be at a maximum when the potential is not zero. Furthermore, a potential may exist at the mercury surface at the maximum of γ, even in the case of capillary inactive substances like sodium sulfate due to the fact that the water dipoles may be oriented at the mercury surface, as Frumkin* has pointed out. A final difficulty is that even if the metal-solution interfacial potential has been reduced to zero, the metal-metal contact potential (the Volta p.d.) will still exist. Thus, Frumkin found that between a mercury capillary electrode and a 41.5 per cent thallium amalgam capillary electrode an e.m.f. of 0.45 v. existed despite the fact that the mercury electrode and the amalgam electrode both had zero charge on their surfaces as determined from the electrocapillary curve.

There seems to be no possible method to determine the interfacial potential between a metal and a solution or between any two phases that are in contact.

Potentials at Air-solution Interfaces.—Guyot and Frumkin† discovered an interesting method for measuring potential changes at the interface, air-solution. The principle of the method is schematically illustrated in Fig. 6. *A* is a special electrode of platinum or some other metal whose surface is covered with a thin coating of a radioactive material such as polonium or ionium. The rays given off in the radioactive disintegration

* A. Frumkin, "Colloid Symposium Annual," Vol. VII, p. 89.

† Guyot, *Ann. physique*, (10) **2**, 506 (1924); A. Frumkin, *Z. physik. Chem.*, **116**, 485 (1925); see also W. D. Harkins and E. K. Fischer, *J. Chem. Phys.*, **1**, 852 (1933).

ionize the few millimeters of air that are found between *A* and *B* and make the air conducting. In this way the resistance of the air gap is diminished, and a current can flow through the solution at *B* across the air gap to the electrometer, thereby enabling the surface potential to be measured. Of course, the measured e.m.f. also includes other potentials, but these may be held constant while the potential at the air-solution interface is varied. The apparatus can measure, therefore, a change in potential as the surface of the solution is changed.

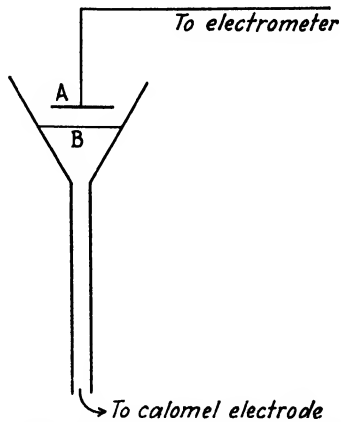


FIG. 6.—Apparatus for measuring air-solution interface potentials.

Frumkin was interested in measuring the e.m.f. as the aqueous solution was covered with different amounts of various organic substances. The aqueous solution in certain cases was 0.01 *N* hydrochloric acid, and a drop of a compound like myristic acid was spread on the surface of the water. The potential of the surface in reference to the potential without any of the organic

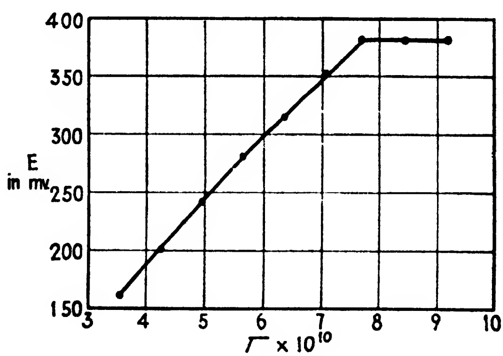


FIG. 7.—Potential curve for myristic acid.

acid on the surface steadily increased until the surface became completely covered or saturated. Further addition of myristic acid to the surface produced no increase in the potential. This behavior, which is typical, is illustrated in Fig. 7. The abscissa

in Fig. 7 is surface concentration; that is, the amount adsorbed per unit of surface (moles per square centimeter). Frumkin* has also used an electrostatic method to determine the effect of ions in solution upon the surface potential. He was able to show "that the surface of many salt solutions are negatively charged at higher concentrations compared to pure water, indicating the presence of an excess of anions in the outer part of the surface layer." These results are in accord with the deductions from the electrocapillary curves and are also in agreement with measurements of surface tension.

Lark-Horovitz and Ferguson,† using Guyot's method, have shown that the surface of an aqueous solution acts partially as a hydrogen electrode provided the surface is covered with a monomolecular layer of stearic or oleic acid. In alkaline solutions the monomolecular layer appears to behave somewhat like a sodium electrode. Lark-Horovitz and Ferguson conclude "the phenomena observed with these layers present a striking analogy to the phenomena observed with glass, quartz, and paraffin films."

At this time, however, the exact interpretation of the observed e.m.fs., is still uncertain. The interfacial potential is not a ζ-potential, and it is doubtful if it is a thermodynamic or Nernst potential. At present we must call them simply "contact potentials" and hope that more investigations in the future will spread greater light on the interesting problem of the exact nature of these contact potentials.

* A. Frumkin, "Colloid Symposium Annual," Vol. VII, p. 91 (1930).

† K. Lark-Horovitz and J. E. Ferguson, *Bull. Amer. Phys. Soc.*, **7**, No. 5, 11 (1932).

CHAPTER XXVIII

IRREVERSIBLE ELECTRODE PHENOMENA

Introduction.—The e.m.fs of a galvanic cell that are measured in a reversible way, *i.e.*, with no current flowing through the cell, can be treated by purely thermodynamical methods and for this reason lead to results of great theoretical significance. If, however, a current of any appreciable magnitude flows through the cell, the e.m.f. changes, the electrodes become "polarized," and the potentials are no longer reversible potentials but are irreversible. Irreversible potentials are a new type of potential; they are different from other types studied hitherto, such as reversible potentials, phase-boundary and semipermeable-membrane potentials, and ζ-potentials. Irreversible electrode phenomena are of great importance technically. In all industrial electrochemical operations it is necessary to pass significant currents of electricity through the cell, thus causing the potentials at the electrodes to be irreversible potentials. For this reason the electrical energy consumption, which is a large factor in the cost of industrial operations, is determined by the irreversible e.m.f. of the cell and not by the thermodynamic e.m.f.; technical electrochemists are interested, therefore, chiefly in the irreversible voltage of their cell in operation.

Irreversible electrode phenomena have also been studied from a theoretical standpoint in the hope that the elucidation of these effects will lead to a better understanding of the mechanism of reactions at the electrodes. In the last few years, thanks to the quantum mechanics, a real beginning in the solution of the problem of irreversible potentials has been attained, so that now even greater theoretical interest is attached to them.

Although there has been a vast amount of research in the field of irreversible phenomena, it must be admitted that in most cases the experimental conditions have been so poorly defined that the results have only qualitative significance. The widely divergent data of the different investigators have, of course, led to widely

divergent theories, the net result being that the whole subject of polarization and overvoltage is much confused.

Concentration Polarization.—Polarization has already been described and mathematically defined in Chap. XII. In this chapter, however, we cannot attach the precise meaning of polarization as used in Chap. XII to polarization of electrodes, because we are largely ignorant concerning the exact nature of electrode mechanisms. Polarization in this chapter is to be conceived as the production of any irreversible potential at the surface of an electrode; an electrode which exhibits its proper reversible potential when immersed in a solution of its ions is not polarized. This definition of polarization which is based on irreversibility of the electrode mechanism does not, however, include an effect which generally goes under the name of concentration polarization. The author believes that concentration polarization is a misnomer inasmuch as the electrode potentials are not irreversible in this case, but reversible.

Consider two reversible copper electrodes immersed in a copper sulfate solution. Initially the e.m.f. between the two electrodes is zero. Let a current be passed through the cell until a definite concentration change has taken place around each electrode. At the electrode which is made positive by the applied e.m.f. copper ions will go into solution, causing the solution in the immediate neighborhood of the electrode to become more concentrated in copper ions. At the cathode, or negative electrode, copper ions will be deposited on the electrode, causing the solution in the immediate neighborhood of the cathode to become less concentrated in copper ions. If the current is now stopped and the resulting e.m.f. between the two electrodes measured, the e.m.f. will be no longer zero but will have a value which depends upon the relative copper ion concentrations at the two electrodes. In other words, the electrolysis of the solution has produced a concentration cell, and the observed e.m.f. is that of a copper ion concentration cell with liquid junction. It is obvious that the difference in potential between the two electrodes will become greater the longer the current flows, but it must be remembered that the amount of copper ions which accumulates around any one electrode depends upon the transference number of the copper ion. Although the difference in potential between the two

electrodes is given by the familiar equation

$$E = \frac{RT}{2F} \ln \frac{c''_{Cu^{++}} f''_{Cu^{++}}}{c'_{Cu^{++}} f'_{Cu^{++}}}, \tag{1}$$

the measured e.m.f. will not agree with Eq. (1) owing to the presence of liquid-junction potentials that are produced in the body of the solution.

The electrodes can hardly be said to be polarized since if they were replaced by two reversible copper electrodes, the measured e.m.f. would be exactly the same. In other words, concentration polarization, which can be easily eliminated by stirring the electrolyte, is nothing abnormal and comes within the realm of thermodynamics. It is possible, however, to polarize an electrode by the passage of a very small amount of electricity. In this case the change of concentration of the ions in the immediate neighborhood of an electrode is insufficient to produce the large electrode potential that is observed; furthermore the potential cannot be reduced by stirring. In addition to the possibility of polarizing an electrode by the flow of a small amount of electricity, it is also possible that the electrode may be polarized only *during* the flow of current. Both of these effects are irreversible phenomena, and as such will be studied in the next section.

Overvoltage.—Any potential in excess of the reversible potential of an electrode is defined as overpotential or, as it is more frequently called in America, *overvoltage.* If a bright platinum electrode, let us say, is immersed in a $N/5$ sulfuric acid solution which has been freed of all dissolved oxygen by bubbling purified hydrogen through the solution and if the sulfuric acid solution is connected to a saturated calomel electrode and the e.m.f. measured, the observed value of the platinum-electrode calomel-electrode cell will be that of a reversible galvanic cell and will be the proper thermodynamic value, approximately -0.3 v. (taking the sign of the platinum electrode). But if a small direct current is allowed to flow across the platinum electrode (but not across the calomel electrode) in such a direction as to liberate gaseous hydrogen at the platinum, the measured e.m.f. between the platinum and the calomel electrode will become more negative, and an overvoltage will result. The magnitude of the overvoltage depends upon the current that flows across the electrode, or rather upon the current density. If the sulfuric acid

solution is saturated with oxygen instead of hydrogen in order to obtain an oxygen electrode (this is only theoretically possible), the observed e.m.f. of the platinum electrode in reference to the calomel electrode would be about +0.9 v. On the passage of a finite current across the oxygen electrode, in a direction to liberate oxygen, the measured e.m.f. becomes more positive than 0.9, and an overvoltage results. These relationships are expressed in Fig. 1, in which the shaded portions represent regions of definite overvoltages on the electrodes. The solid lines represent reversible e.m.fs. of the hydrogen and oxygen electrodes and the area between the solid lines represents potentials of the electrode as it is making a transition from the potential of an oxygen electrode to the potential of a hydrogen electrode. Abscissas do not represent any particular quantity in Fig. 1; later on, we shall plot time, temperature and perhaps other quantities on the abscissa, but this is not necessary here.

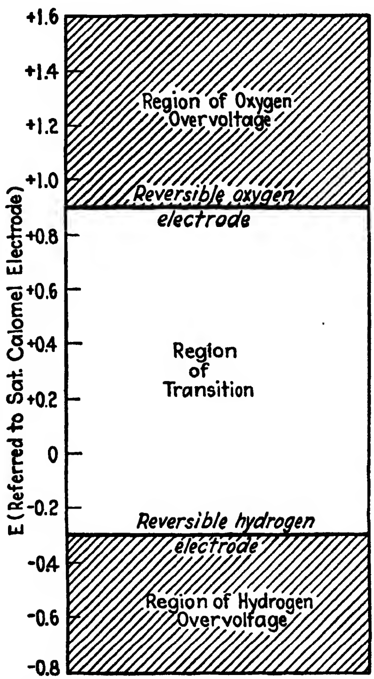


FIG. 1.—Schematic diagram to explain overvoltage.

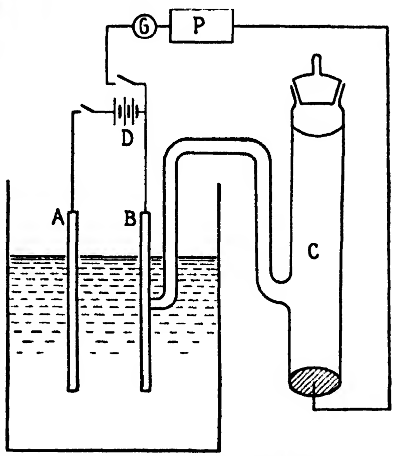


FIG. 2.—Apparatus for measuring overvoltage by the direct method.

Concentration polarization plays no part in causing overvoltage. We can assume that the solutions are stirred vigorously enough to eliminate any concentration gradient in the cell.

There are several methods for measuring overvoltage at the surface of an electrode; those most frequently used are the direct method and the commutator method. The essential parts of an apparatus for measuring overvoltage directly are shown in Fig. 2, in which *A* and *B* are two electrodes immersed in the electrolyte, *C* is the calomel electrode whose side arm is immersed in the electrolyte close to electrode *B*. A direct current generated by the battery *D* is passed through the circuit *ABD* in order to polarize the electrode *B*. The extent of polarization of *B*, or the overvoltage of *B*, is determined by measuring the e.m.f. of the circuit containing the calomel electrode *C*, the potentiometer *P*, and the galvanometer *G*. The overvoltage is equal to the measured e.m.f. minus the e.m.f. of the same circuit when no current is flowing through the polarizing circuit *ABD*, or in other words, when the potential at electrode *B* is at its proper reversible value. This method has the advantage that the overvoltage of a single electrode may be measured, and there are reasons mentioned below which lead one to believe that the direct method is the only method by which results of any theoretical significance can be obtained.

The commutator method does not measure the overvoltage while the direct current is flowing across the electrode-solution interface, but shortly after the circuit *ABD* of Fig. 2 has been opened. The commutator is a device for connecting the polarizing circuit for a definite time interval and then the potentiometer circuit for another definite time interval, but the details of the apparatus will not be described here.* Tartar and Keyes† designed an apparatus which enabled them to measure overvoltage simultaneously by the direct and commutator methods. Some of their results are given in Table I which illustrates the difference in the results obtained by the two methods.

Glasstone‡ arranged a commutator apparatus so that he could measure the e.m.f. of the calomel electrode-polarized electrode circuit 0.002, 0.004, 0.006, and 0.012 sec. after the current in the polarizing circuit was broken. On extrapolation of his e.m.f. values back to zero time, he obtained practically the same results

* See Knobel, *J. Amer. Chem. Soc.*, **46**, 2613 (1924).
† Tartar and Keyes, *J. Amer. Chem. Soc.*, **44**, 557 (1922).
‡ S. Glasstone, *J. Chem. Soc.*, **125**, 250 (1924).

as with the direct method. However, Glasstone's experiments do not solve the problem concerning the moment at which to measure the overvoltage; *i.e.*, is the overvoltage to be calculated from the e.m.f. at zero time or at some other time interval after the polarizing circuit is opened? Thus, Newbery* believes that the rapid fall of potential on opening the polarizing circuit proves the existence of a "transfer resistance" at the electrode surface which causes the overvoltage as measured by the direct method to be too high. He believes that the potential fall through the transfer resistance should not be included in overvoltage.

TABLE I.—OVERVOLTAGES ON COPPER CATHODES IN VOLTS

Current density, amp./sq. dcm.	Commutator method	Direct method
0.26	0.456	0.563
0.39	0.454	0.619
0.64	0.475	0.690
1.27	0.475	0.832

Ferguson and coworkers† who have carried out an extensive study of overvoltage criticize the commutator method stating that electrode potentials as measured decrease with increase in the r.p.m. of the commutator due to increase in brush contact resistance. They succeeded in devising an oscillograph commutator system which enabled them to measure the electrode potential 0.0001 sec. after the circuit is broken. They find no difference in maximum overvoltage recorded between the direct and commutator method insofar as anode overvoltages are concerned; cathode overvoltages are slightly less by the commutator method, at least at low current density, but not at higher. They find no evidence of a "vertical" drop in the e.m.f.-time curve at the beginning of the discharge interval such

* NEWBERY, *J. Chem. Soc.*, **125**, 511 (1924).

† A. L. FERGUSON and G. M. CHEN, *J. Phys. Chem.*, **36**, 1156, 1166, 2437 (1932); FERGUSON and VAN ZYE, *Trans. Electrochem. Soc.*, **47**, 227 (1925); FERGUSON and DUBPERNELL, *ibid.*, **64**, 221 (1933).

as would be required by the presence of a transfer resistance. They have also measured the overvoltage at the back of an electrode and find that none exists.

Other factors which have been thought by investigators to affect overvoltage are:

1. Condition of electrode surface. The overvoltage is lower the rougher the electrode surface.

2. Purity of electrode metal. An impurity existing even to the extent of a trace may considerably alter the overvoltage.

3. Length of electrolysis. Maximum hydrogen overvoltage on smooth platinum is sometimes reached only after 5 hr. of electrolysis.

4. Temperature change. Increase of temperature has been shown by some authors to lower overvoltage, by others to raise overvoltage or by still others not to change it at all.

5. Presence of colloids. The overvoltage is increased by the presence of colloids.

6. Effect of ultraviolet light. The electrodeposition of hydrogen and oxygen is accelerated by exposure of the electrodes to light of short wave length.

7. Superimposition of alternating current. The overvoltage is lowered.

8. Time. Overvoltage may increase or decrease with time.

9. Surface tension. No definite relation between surface tension and overvoltage can be stated.

10. Pressure and pH. Hydrogen overvoltage is independent of pH and external pressure.

Similarly we can list the various theories that have been invented to explain hydrogen overvoltage:

1. Overvoltage is due to potential drop across film of hydrogen at electrode.

2. Transfer resistance at electrode accounts for part of overvoltage.

3. Accumulation of some material such as atomic hydrogen, molecular hydrogen, negative hydrogen ions, hydrogen dipoles, etc., produces a "back" e.m.f. or e.m.f. which is opposed to the applied e.m.f. and thus increases the overvoltage.

4. Overvoltage is related to surface forces and ease of formation of gas bubble at surface of electrode.

5. Inability of the electrode to catalyze the reaction $2H \rightleftarrows H_2$ increases overvoltage.

6. Overvoltage is due primarily to the speed of the reaction $2H^+ + 2\epsilon^- \rightarrow H_2$.

7. Overvoltage is due to the formation of metallic hydrides on electrode surface.

8. Overvoltage is a necessary consequence of the nature of metals.

Unfortunately we have space here for a description of only a few of the interesting experiments which have been performed on overvoltage. Some of the more recent experiments are those of Bowden and it is these experiments which have been selected for discussion.

Bowden's Experiments on Overvoltage.—Using a new method Bowden, and Bowden and Rideal,* made a comprehensive study of hydrogen and oxygen overvoltage. They rejected the commutator method as unsuitable since it measures the average of a large number of cycles and not the initial growth and decay of the overvoltage. They decided that it would be much better to start with a reversible hydrogen electrode that has not been polarized and then measure the overvoltage the first instant that the direct current begins to polarize the electrode. To accomplish this purpose they designed the apparatus illustrated in Fig. 3, the details of which are as follows:

A number of small storage batteries of 50 v. total voltage served as the source of the polarizing current, while a variable resistance of several million ohms enabled the current strength to be regulated at will. The microammeter S and the milliammeter R measured the smaller and larger currents, respectively. P was the test electrode, the cathode in Fig. 3, while the anode was purely an auxiliary electrode which enabled the polarizing circuit to be completed. The e.m.f. developed between the test electrode P and the calomel electrode Q was measured by the usual potentiometer arrangement with the important exception that an Einthoven string galvanometer replaced the d'Arsonval galvanometer. The string galvanometer was used in order to

* F. P. Bowden and E. K. Rideal, *Proc. Roy. Soc.*, A **120**, 59 (1928); Bowden, *ibid.*, A **125**, 446 (1929); A **126**, 107 (1929); Bowden and O'Connor, *ibid.*, A **128**, 317 (1930).

obtain practically instantaneous measurements of the e.m.f. The period of the galvanometer was $\frac{1}{300}$ sec., and the e.m.f. could be measured to the nearest millivolt. In Fig. 3, light from a powerful lamp *A* was focused by means of the condensing lenses *B* and *C* on the fiber or string of the galvanometer *D*. The shadow of the fiber was magnified by the microscope *E*, condensed by the lens *F* (without changing the horizontal magnification), and finally allowed to fall on the moving-film camera *H*.

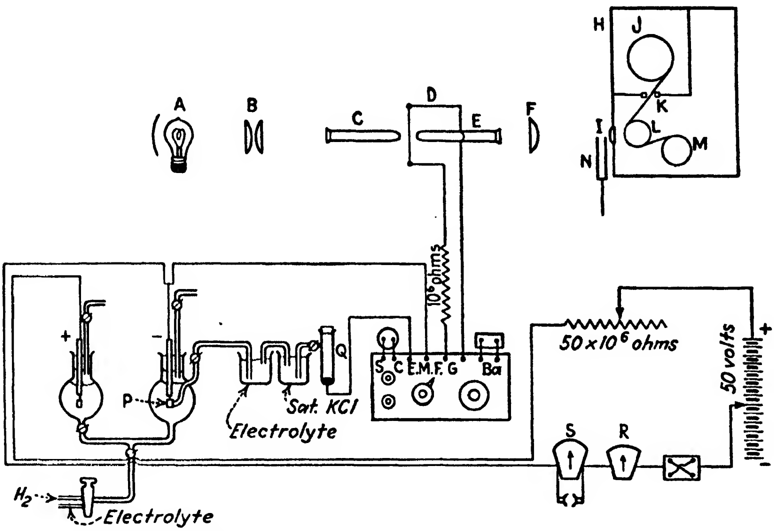


FIG. 3.—Apparatus of Bowden and Rideal for measuring overvoltage

The cylindrical lens *I* focused the beam of light on to the sensitive photographic film which was run by clockwork across the opening of the camera by means of the rollers *J*, *L*, and *M*. *K* was a spring slit which maintained a constant tension on the paper. The timing was given by the electrically driven tuning fork *N* which vibrated in front of the lens *I*, thereby throwing a shadow on the photographic film.

Bowden and Rideal used *N*/5 sulfuric acid as the electrolyte in most of their experiments. In the measurement of hydrogen overvoltage, the sulfuric acid was freed of oxygen by prolonged boiling of the solution under reduced pressure, followed by cooling in a hydrogen atmosphere. The apparatus was so arranged

(Fig. 3) that the electrolyte could be run into the cell without coming in contact with air. This last precaution is very important inasmuch as Bowden and Rideal found that the electrode phenomena were different depending upon the presence or absence of oxygen. This is clearly shown in Fig. 4 where the e.m.f. of a silver electrode in $N/5$ sulfuric acid as measured against the saturated calomel electrode is plotted as a function of the time as a current of 0.00025 amp. per square centimeter was passed

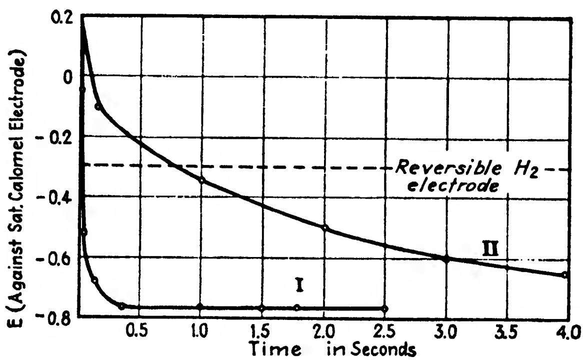


FIG. 4.

through the polarizing circuit. Curve I represents the observed e.m.f. in the oxygen-free atmosphere, while curve II represents the values in a $N/5$ sulfuric acid solution in which no attempt was made to free the solution of oxygen.

On opening the polarizing circuit and allowing the potential to "decay," *i.e.*, to fall, the results also depend upon the presence or absence of oxygen.

Bowden* has also pointed out that if there are any metallic ion impurities in the solution which deposit on the cathode during electrolysis, errors in overvoltage will result. According to Bowden, the results of Newbery† which led Newbery to postulate his "metallic hydride" theory were really due to dissolved metallic ion impurities.

Bowden and Rideal first determined the variation of potential of different electrodes as the polarizing circuit was initially closed. Their results for a purified mercury electrode are given in Fig. 5.

* *Trans. Faraday Soc.*, **23**, 571 (1927).

† NEWBERY, *Proc. Roy. Soc.*, A **111**, 182 (1926).

The initial e.m.f. is approximately −0.3 v.; any value more negative than this represents overvoltage of the mercury electrode. At the time indicated in Fig. 5, the polarizing circuit was closed, thereby allowing a current of density 4×10^{-5} amp. per square centimeter to flow. The e.m.f. immediately became more negative as indicated in the figure until a constant value of nearly −1.1 v. was obtained. It is interesting to note that the initial change of potential varies linearly with the time and it is

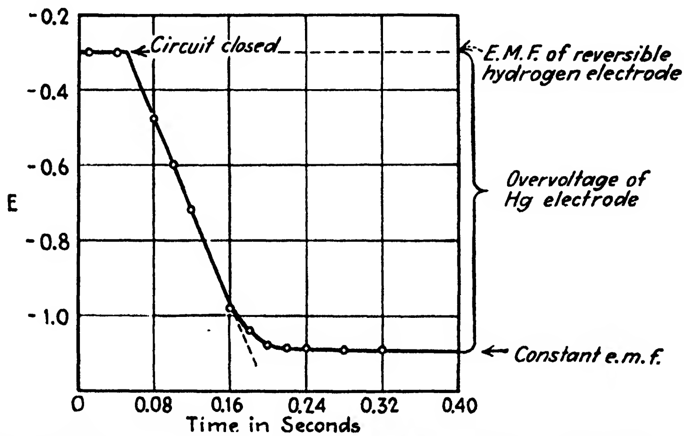


FIG. 5.—E.m.f. of mercury electrode measured against saturated calomel electrode as a function of the time.

also interesting to note that the potential of the electrode becomes constant in 1/5 sec. The whole time interval represented by Fig. 5 is only 1/3 sec.

Bowden and Rideal point out that the initial variation in e.m.f. is a linear function of the time, or since time × amperes = coulombs, the electrode potential initially varies linearly with the total number of coulombs passed through the cell. Actually they find that the number of coulombs necessary to change the potential 100 mv. is exceedingly small, being only 6×10^{-7} coulomb per square centimeter of electrode surface. This value is the same for all smooth surfaces, as tests on mercury, amalgamated silver, liquid alloy (approximating Wood's metal) and liquid gallium proved. A much larger number of coulombs per square centimeter is required to change the potential by 100 mv. if the surface is roughened as in etched or sandpapered

silver, platinized platinum electrodes, etc. Bowden and Rideal ascribe this fact to an increase in the accessible area of the electrode.

Bowden and Rideal also carried out some experiments which confirm the figure 6×10^{-7} coulomb per square centimeter necessary to change the potential 100 mv. On reversing the direction of the polarizing current the e.m.f. immediately falls, the decline of potential equal to 100 mv. is produced by the passage of exactly 6×10^{-7} coulomb per square centimeter, the same number of coulombs necessary to polarize the electrode to the extent of 100 mv. Thus, whether the electrode is being polarized or depolarized, the passage of the same amount of electricity produces the same change in potential. This is true if no oxygen is present in the cell; if oxygen is present, the two methods of determining the number of coulombs per 100 mv. change of potential give widely different results. In this way, Bowden and Rideal have proved the reliability of their data.

Before taking up the results of their measurements of overvoltage, it is interesting to point out that the initial linear variation of potential with time or number of coulombs is exactly what one would obtain with a condenser. When an external e.m.f. is applied to a condenser, electricity flows into the condenser; the voltage across the condenser being given by the equation [Chap. XI, Eqs. (4) and (7)]

$$E = Q\frac{4\pi d}{DA},$$

where d is the distance between the plates of the condenser, A is the area of cross section, D the dielectric constant, and Q the number of coulombs which have flowed into the condenser.

When the overvoltage becomes constant, hydrogen must be leaking off the electrode in accordance with Faraday's law. Bowden and Rideal found that by plotting the constant overvoltage values against the logarithm of the current density, a straight line was obtained. Not only were straight lines obtained for all the different types of electrodes studied, *but the slopes of the lines proved to be equal to the same value.* These important facts are illustrated in Fig. 6 where overvoltage values for different current densities are plotted as a function of the logarithm of the apparent current density.

Apparent current density means that the measured area of the electrode was assumed to be its true area. For etched silver, polished silver, and bright platinum the actual surface area is somewhat greater than the apparent area because the surface is increased by roughness. Bowden and Rideal point out how the true current density may be calculated by measuring the number of coulombs necessary to raise the e.m.f. 100 mv.

The linear relationship between the overvoltage V and the logarithm of the current density $\mathbf{i}$ had been discovered in 1905

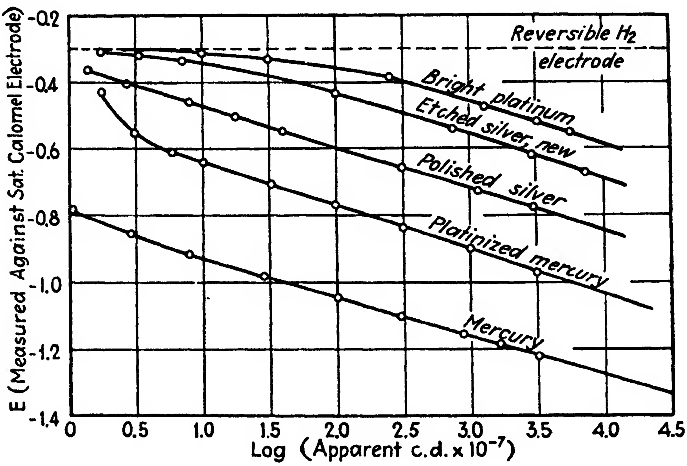


FIG. 6.

by Tafel* for mercury surfaces, but Bowden and Rideal found that it also was true for surfaces of platinized mercury, silver, and platinum.

Continuing his study of overvoltage, Bowden measured the temperature coefficient of overvoltage in order to find the variation of the slope of the lines of Fig. 6 with change of temperature. He discovered that the slope of the curves, $\frac{-d \log \mathbf{i}}{dV}$, was inversely proportional to the absolute temperature. In Fig. 7 the measured e.m.f. against a saturated calomel electrode of a mercury electrode in hydrogen at the constant current density of 1×10^{-5} amp. per centimeter squared is plotted as a direct

* TAFEL, *Z. physik. Chem.*, **50**, 641 (1905).

function of the centigrade temperature. This is, of course, equivalent to plotting $\frac{-d \log i}{dV}$ against the reciprocal of the absolute temperature. Apparently, the overvoltage decreases slightly with rise of temperature. In order to clarify the observed

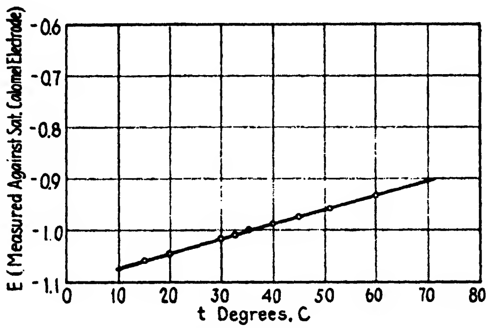


FIG. 7.—Cell measurements at a constant current density of 1×10^{-5} amp. per square centimeter as a function of the centigrade temperature.

relationships, Bowden introduced a constant, α, given by the equation

$$\alpha = -2.3RT\frac{d \log i}{dV} \tag{2}$$

(R equals here 8.6×10^{-5} volt farad).
In Eq. (2) R is the gas law constant, T is the absolute temperature, i is the current density in amperes, and V is the overvoltage in volts ($V = E - E_0$, where E_0 is the reversible e.m.f. of the electrode). Some data obtained by Bowden for α are given in Tables II and III.

TABLE II.—HYDROGEN OVERVOLTAGES ON MERCURY

T	$\frac{-d \log i}{dV}$	α_H
273	9.2	0.50
309	8.1	0.49
345	7.1	0.50

Apparently the constant α for hydrogen is independent of the temperature and the nature of the surface. Surfaces of mercury

TABLE III.—HYDROGEN OVERVOLTAGES ON VARIOUS METALS

Metal	α_H
Polished silver	0.50
Etched silver	0.51
Polished nickel	0.52
Rolled nickel	0.51
Annealed nickel	0.52
Electroplated nickel	0.50

contaminated by depositing platinum electrolytically did not give values of α_H equal to 0.5, nor did new platinum electrodes. Bowden points out that very prolonged electrolysis may deposit impurities from the solution and thus contaminate the surface, lowering the value of α_H. Bowden also found that hydrogen overvoltage is independent of the pH of the electrolyte within the pH limits 0.9 to 6.6; at high current densities or at high pH values, the value of α_H may fall to 0.25, however.

Very interesting results were obtained by Bowden* when the current of the polarizing circuit (Fig. 3) was run in a direction to evolve oxygen from the test electrode *P*. Experiments were carried out both in oxygen and in hydrogen atmospheres, the general type of results being shown in Fig. 8, which illustrates the results in hydrogen atmospheres, and in Fig. 9 which illustrates the results in oxygen atmospheres.

At the point *A*, Fig. 8, the platinum electrode which had been serving continuously as a cathode in a hydrogen saturated solution is suddenly made anodic. The potential becomes rapidly more positive to that of the reversible hydrogen electrode, then more slowly to the point *B* at +0.37 v. where there is a slight arrest in the curve. Continued passage of a current having a current density of 2.5×10^{-2} amp. per centimeter squared causes the e.m.f. to rise rapidly to the high overvoltage value of oxygen on platinum point *C*. After maintaining the e.m.f. at +1.8 v. for an instant the current is reversed and the test electrode again made cathodic. The e.m.f. falls from +1.8 to +1.2 v., point *D*, while the switch is being thrown over, and then falls linearly during the passage of the current to +0.37, at which voltage there was no change of e.m.f. for a comparatively long time (less than a second, however). Finally, at the point *F*, the e.m.f. falls linearly to that of the reversible hydrogen elec-

* F. P. BOWDEN, *Proc. Roy. Soc.*, A **125**, 446 (1929).

trode. Bowden found that the length of time that the e.m.f. paused at +0.37 v. depended upon the length of time that the platinum electrode had been made anodic; if the electrode had been made anodic for 10 sec., the pause at +0.37 v. lasted 50 sec.

For platinum electrodes in oxygen atmospheres the behavior is somewhat different (Fig. 9). Starting with a platinum electrode which had been an anode in an oxygen atmosphere, the current is

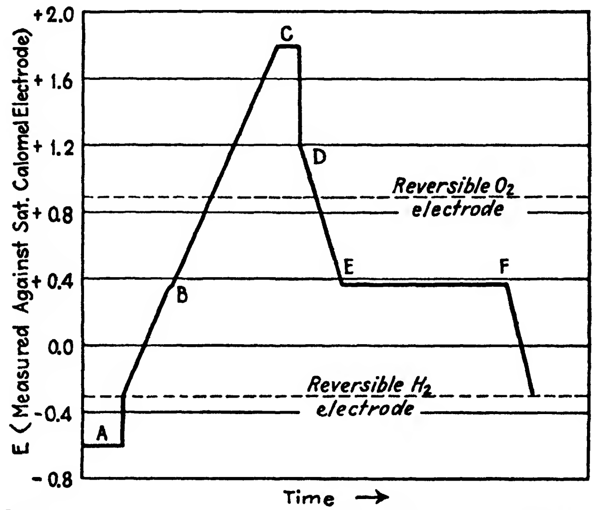


FIG. 8.—Oxygen overvoltage on platinum in hydrogen atmospheres. Figures 8 and 9 are schematic since the abscissas are not drawn to scale.

suddenly reversed (point A), causing the e.m.f. to fall rapidly to +0.9 v. (point B), and then more slowly to +0.37 v. (point C), where the e.m.f. made a long pause. At the point D the e.m.f. fell linearly to the reversible e.m.f. of the hydrogen electrode. After a few seconds at −0.3 v., the circuit was opened so that no polarizing current flowed through the cell. The e.m.f. paused for a moment at −0.3 v. and then rose rapidly to +0.62 v., point F, where the e.m.f. remained constant indefinitely.* The

* J. A. V. Butler and G. Armstrong, *Trans. Faraday Soc.*, **29**, 862 (1933), find that if a bright platinum electrode is made anodic for a short interval and then cathodic for an instant, the electrode gives a much more reproducible potential and may be used to obtain excellent acid-base titration curves. It is possible that their electrodes correspond to the condition represented by the line FG of Fig. 9 See also Butler and Armstrong, *Proc. Roy. Soc.*, A **137**, 604 (1932).

length of time that the e.m.f. paused at -0.3 v. after the circuit was opened depended upon the length of time that the electrode had been made cathodic. The oxygen overvoltage on platinum was finally restored by closing the polarizing circuit again (point *G*); the e.m.f. rose linearly to $+1.8$ v. These experiments not only showed that Bowden's general method may be applied to the measurement of oxygen overvoltage, but they also revealed the existence of the "arrests" in the curves at $+0.37$ and $+0.62$ v. Bowden attributes these arrests in the curve to the formation of

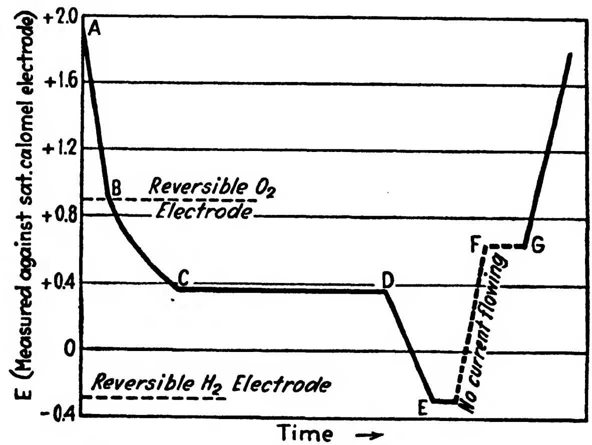


FIG. 9.—Oxygen overvoltage on platinum in oxygen atmospheres.

an oxide of platinum, probably PtO_2, on the surface of the electrode. A platinum wire mechanically coated with PtO_2 by Bowden gave an e.m.f. value of $+0.62$ v. in an oxygen atmosphere and $+0.38$ v. in a hydrogen atmosphere. These values coincide

TABLE IV.—OXYGEN OVERVOLTAGES ON PLATINUM

T	$\frac{d \log i}{dV}$	α_0
273	10.0	0.54
287	8.7	0.49
308	8.0	0.49
330	7.7	0.50
354	7.0	0.49
...	....	Mean (0.50)

almost exactly with the e.m.f. of the platinum electrode at the two arrest points.

Oxygen overvoltages as a function of current density and of temperature were also investigated by Bowden. He discovered the important fact that identical values of α were obtained for oxygen overvoltages and for hydrogen overvoltages. Table IV gives his data which should be compared with the results for hydrogen overvoltages listed in Table II.

Bowden's experimental results, some of which have not been described, can be summarized as follows:

1. Initially, the hydrogen overvoltage on mercury rises 1 v. for every 3.7×10^{13} electrons that flow through the polarizing circuit (6×10^{-7} coulomb per square centimeter per 100 mv.).

2. For the constant overvoltage values, the overvoltage and the current density are related by the equation

$$\frac{d(\log i)}{dV} = \frac{A}{T}, \tag{3}$$

where A is a constant.

3. Despite the fact that it is oxygen that is discharged at the anode and hydrogen at the cathode, anodes and cathodes of platinum give the same value of A, 1.7×10^6 if V is expressed in electrostatic units. Cathodes of silver, mercury, nickel, and platinum also give the same value of A.

4. At constant overvoltage, the relation between the current density and the temperature is given by the equation

$$\frac{d(\log i)}{dT} = B, \tag{4}$$

where B is a constant, having a value between 0.05 and 0.06 depending upon the overvoltage.

Bowden's results may be summarized by the equation

$$I = -k\ exp\left(-0.5\frac{FV}{RT}\right), \tag{5}$$

where I is the current, k is a constant and independent of the hydrogen ion concentration but a function of the temperature and nature of the cathode metal.

Hammett* has shown that for currents at very low overvoltages such as on catalytically active platinum the current is given by the equation

$$I = k\left\{1 - exp\left(-\frac{2FV}{RT}\right)\right\}, \tag{6}$$

where V is limited to the values $-0.01 < V < +0.01$. The consensus of opinion† seems to be that Bowden's or Tafel's equation (5) is to be explained by the rate of the forward part of the reaction

$$H^+ + \epsilon^- \rightleftarrows H. \tag{7}$$

Hammett‡ gives an equation for the current which combines Eqs. (5) and (6) and which takes into consideration the rate of the reaction

$$2H \rightleftarrows H_2. \tag{8}$$

Apparently the rate of the forward reaction of Eq. (7) determines the current when the overvoltage is high as in Bowden's work while the rate of the forward reaction of Eq. (8) determines the current when the overvoltage is low as in Hammett's work.

These theories of overvoltage do not, of course, explain all the effects that have been observed by different investigators. These latter effects are chiefly produced by comparatively high current densities where physical considerations in addition to those proposed will have to be brought into the picture. MacInnes and Adler§ discovered that, at constant current density, the overvoltage undergoes a periodic variation, corresponding to the formation and release of a gas bubble. This fact seems to indicate that the amount of gas accumulated on the electrode has an effect on overvoltage. The question of liberation of gas at an electrode brings us to a consideration of *decomposition voltage.*

Decomposition Voltage.—If the current density is plotted as a function of the applied e.m.f., a sudden break in the curve will

* L. P. HAMMETT, *J. Amer. Chem. Soc.*, **46**, 7 (1924).

† See Gurney's quantum mechanical theory of overvoltage in the next chapter. Also Erdey-Grúz and Volmer, *Z. physik. Chem.*, **150A**, 203 (1930); A **162**, 116 (1932).

‡ L. P. HAMMETT, *Trans. Faraday Soc.*, **29**, 770 (1933).

§ D. A. MACINNES and ADLER, *J. Am. Chem. Soc.*, **41**, 194 (1919).

appear at a point equal to the decomposition voltage. Above this point, the current density increases very rapidly with increase of applied e.m.f. This is shown schematically in Fig. 10. Decomposition voltages, E_d, appear at higher current densities than those which Bowden was interested in. At current densities greater than the value corresponding to E_d, the current density is directly proportional to the applied e.m.f. Le Blanc* was the first to measure decomposition voltages, and he discovered that they were practically identical for most acids and bases studied, but that the decomposition voltages of salt solutions varied widely. From this he concluded that in the case of acids and bases, the decomposition voltage measured in every case the voltage necessary to decompose water, and for this reason they were identical. The decomposition voltages of hydrochloric acid as a function of concentration are interesting, Table V. The values indicate that in concentrated solutions

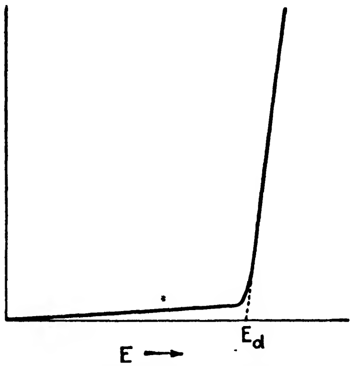


FIG. 10.—Schematic representation of current density-voltage curve.

TABLE V.—DECOMPOSITION VOLTAGES OF HYDROCHLORIC ACID

Concn.	E_d
2	1.26
½	1.34
⅙	1.41
1/16	1.62
1/32	1.69

HCl is being decomposed (H_2 and Cl_2 liberated at the electrodes), while in dilute solutions H_2O is being decomposed (H_2 and O_2 liberated at the electrodes). This is because the decomposition potential of water is about 1.7 v., and that of hydrochloric acid is considerably lower. Evans, Lee, and Lee† electrolyzed ether

* M. LE BLANC, *Z. physik. Chem.*, **8**, 299 (1891). "A Text-Book of Electrochemistry," Chap. VIII, The Macmillan Company, 1907.

† W. V. EVANS, F. H. LEE, and C. H. LEE, *J. Am. Chem. Soc.*, **57**, 489 (1935).

solutions of methyl and ethyl magnesium bromide obtaining the results illustrated in Fig. 11 where galvanometer readings (which are proportional to current density) are plotted against the voltages of the cell. The sharp break in the curves indicates the decomposition voltages. It is interesting to observe that the decomposition voltages are different for the different Grignard reagents. Other Grignard compounds were also investigated.

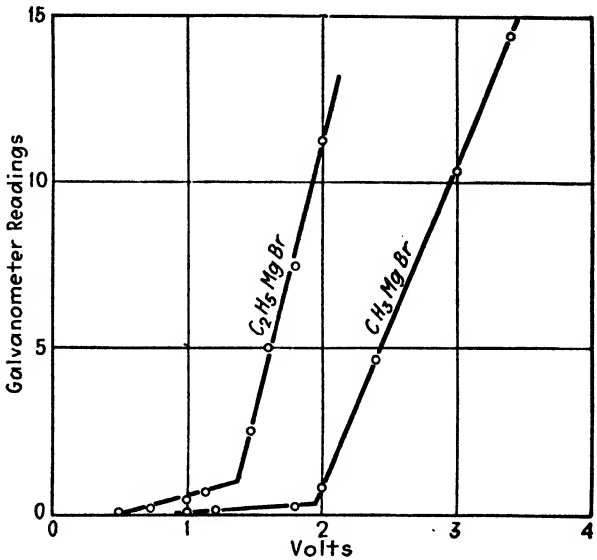


FIG. 11.

Passivity.—Probably every chemist has noticed sometime in his career the difficulty with which iron dissolves in nitric acid. When a piece of iron is placed in nitric acid, it dissolves at first as is shown by evolution of gas, but soon the reaction ceases and the iron remains in contact with the nitric acid indefinitely without going into solution. This curious phenomenon in which the iron is said to be in a *passive* state was discovered in 1790 by James Keir and has since been the subject of innumerable investigations. Faraday* in 1836 became interested in passivity and as a result of his studies proposed a theory of the passive state which seems to be the accepted theory today.

* M. FARADAY, *Phil. Mag.*, **9**, 57, 122 (1836); **10**, 175 (1837).

A great many facts have been accumulated concerning passivity; they may be listed as follows:*

1. Iron may be made passive electrically by making it the anode in the following acids: nitric, sulfuric, and phosphoric. When solutions of chlorides, bromides, fluorides, or iodides are used, iron does not become passive.

2. Strong nitric acid and fuming sulfuric acid will make iron passive without electrolysis as will silver nitrate, lead nitrate, potassium permanganate, potassium dichromate, mercuric nitrate, copper potassium tartrate, and ammoniacal copper solutions.

3. Compressed nitric oxide gas can produce passivity in iron while air will make chromium and palladium passive.

4. The time required to produce passivity depends upon strength of acid, current density, and temperature.

5. Chromium can be made passive in hydrochloric, hydrofluoric, hydrobromic, sulfuric, perchloric, phosphoric, and nitric acid at 0°C., but it becomes active in the first four acids if they are warmed.

6. Chromium in zinc chloride solutions becomes passive and dissolves as hexavalent chromium, but at 130°C. it is active and dissolves as bivalent chromium.

7. Iron dissolves slowly even when passive.

8. The active state may be restored by raising the temperature, making the metal the cathode, bringing it in contact with the cathode, by stirring, scratching, or knocking. Rapid rotation of iron wire prevents the iron from becoming passive.

9. The passive state may be destroyed by alternately making and breaking the circuit.

10. In addition to iron, chromium, and palladium many other metals can be made more or less passive.

A great number of papers concerning passivity† have been published recently.

* See the review of the passive state by C. W. Bennett and W. S. Burnham, *J. Phys. Chem.*, **21**, 107 (1917).

† The following reviews of passivity may be consulted: Bennett and Burnham, *J. Phys. Chem.*, **21**, 107 (1917); A. M. Hasebrink, *Z. Elektrochem.*, **34**, 819 (1928); U. R. Evans, *Am. Inst. Mining Met. Eng. Tech. Publ.*, No. 205, (1929); W. J. Müller, *Z. Elektrochem.*, **34**, 571 (1928); R. Müller, *Z. Elektrochem.*, **35**, 459 (1929); H. G. Byers, *J. Am. Chem. Soc.*, **30**, 1718 (1908); W. J. Müller, *Z. Elektrochem.*, **40**, 119 (1934).

Evans and coworkers* have been chiefly interested in the relation between passivity and corrosion. Müller† and coworkers and Fink and Kenny have studied the passivity of chromium.

Among the many theories that have been proposed to explain passivity, the oxide film theory seems to be the most reliable. This theory asserts that since passivity is in general produced under oxidizing conditions, some sort of oxide or oxygen film or layer must cover the metal and thus prevent further solution. The process by which a metal can become passive might be conceived as follows: the first step in formation of the layer‡ consists in the adsorption of the hydroxyl ion. By increasing anodic polarization, the hydroxyl ion goes over into an adsorbed monomolecular oxide or hydroxide layer, finally into a polymolecular layer. In the case of iron we can imagine two tendencies at work: If iron is placed in dilute nitric acid where there are many hydrogen ions (large degree of dissociation), the iron will displace hydrogen and will go rapidly into solution; if, however, the nitric acid is concentrated so that there are few hydrogen ions present but a large concentration of oxidizing nitric acid molecules, the surface of the iron will be oxidized and will be rendered passive. Despite the passivity of the iron, hydrogen ions will attack it very slowly, and in a long period of time an appreciable amount of iron will dissolve.

An objection to the oxide or oxygen film theory, which was the theory proposed by Faraday, was that the surface of the passive iron apparently was identical in optical properties with active iron. Thus, Krüger and Nähring§ could discover no oxide film by means of an x-ray investigation. More recent work, however, seems to show that passive iron and steel surfaces do differ in optical properties from active surfaces. Tronstad||

* U. R. Evans and coworkers, *J. Chem. Soc.*, **1929**, 92, 2651; **1930**, 478, 1361, 1773; *Nature*, **126**, 130 (1930).

† W. J. Müller and coworkers, *Z. Elektrochem.*, **37**, 328 (1931); **36**, 365 (1930); *Monatsh.*, **50**, 385 (1928); **51**, 73 (1929); **52**, 53, 289, 409, 425, 442, 463, 474 (1929); C. G. Fink and F. J. Kenny, *Trans. Electrochem. Soc.*, **60**, 235 (1931); See also E. Müller and coworkers, *Z. Elektrochem.*, **36**, 963 (1930); **37**, 185 (1931).

‡ A. Frumkin and Gorodetzkaya, *Z. physik. Chem.*, **136**, 215 (1928).

§ Krüger and Nähring, *Ann. Physik*, (4) **84**, 939 (1927).

|| L. Tronstad, *Z. physik. Chem.*, A **142**, 241 (1929); *Nature*, **127**, 127 (1931).

measured the state of polarization of light reflected by iron and nickel mirrors, both passive and active, and found that the same changes took place when the metals became passive as when they were exposed to air. He assumed that iron, on electrolysis, went into solution; ferric hydroxide was then precipitated as a colloid. The ferric hydroxide is adsorbed on the metal, forming the protective layer. Additional optical evidence for some sort of protective film seems to be afforded by the microscopical studies of Benedicks and Sederholm.* They etched steel with alcoholic solutions of nitric acid and photographed the etched surfaces through a microscope. They observed patches or "islands" of steel that were unetched while other spots were etched and showed the crystal structure of the steel. They conclude that their results are in agreement with the theory that assumes the formation of a protective film which renders the steel passive.

We may also infer the presence of some sort of film from modern studies of the photoelectric effect. By measuring the emission of electrons from surfaces of metals under the action of light, the work function ϕ of the metal can be determined. A low work function means an active metal. Magnesium has a fairly low work function, but if a trace of air is admitted to the photoelectric cell, the work function rises rapidly to a high value. The magnesium loses much of its activity and becomes more like the noble metals. But as long as the surface of the metal is perfectly uncontaminated, the work function has its normal value; there is no evidence of strain in the metal producing abnormal work functions. Passivity, which is equivalent to a high metallic work function, must be due to the presence of some sort of film. Objections to this theory lie in the fact that passivity over the whole metal surface can be destroyed by scratching or knocking the metal. It seems hard to reconcile these facts with the idea of a firmly adhering oxide or oxygen film. However, a greater knowledge concerning the mechanism by which this film is built up and destroyed may overcome the difficulty of explaining the scratching effect.

Although the consensus of opinion among scientists seems to be that some sort of film must exist, there is considerable doubt as to the exact nature of the film. It is unknown whether the film is a

* C. Benedicks and P. Sederholm, *Z. physik. Chem.*, **138A**, 123 (1928).

definite oxide, whether it is a hydroxide or whether it is merely atomic or molecular oxygen adsorbed on the surface of the metal. Fink and Kenny believe that the surface must be uniform in potential (equipotentialization of the surface) for passivity to be produced. Tronstad's optical measurements indicate that in the case of iron the film is composed of ferric oxide (Fe_2O_3) while the oxide, FeO_2, has been suggested. Hydrated oxides or hydroxides are also possible. In addition to the uncertainty regarding the composition of the film, we also have to answer the question concerning the thickness of the film. Whatever the nature of the film, we know that it must be held rather firmly.

Depolarization.—In the foregoing discussion of decomposition voltages it was pointed out that Le Blanc discovered that nearly all acids and bases required the same voltage, 1.7, to liberate oxygen at the anode and hydrogen at the cathode when an appreciable current passed through the cell. The value of the decomposition voltage necessarily depends upon the pressure at which hydrogen and oxygen are liberated; if the pressure is atmospheric in both cases, the decomposition voltage is 1.7, but if the pressure of oxygen, let us say, is reduced, the decomposition voltage falls to a lower value. The pressure of oxygen may be reduced by admitting into the cell some substance which will react with the oxygen as the oxygen is formed on the electrode. Acetylene, for example, has the property of reducing the decomposition voltage of potassium hydroxide from 1.7 to 1.2 v. because it reacts with the oxygen liberated at the anode to form formic acid.* At the decomposition voltage of 1.2, no oxygen is evolved, but if the applied e.m.f. is raised above 1.7 v., oxygen will be evolved simultaneously with its reaction with acetylene. Substances such as acetylene which can be oxidized at anodes are known as *anodic depolarizers*, while substances which can be reduced at cathodes are known as *cathodic depolarizers*. Inorganic examples of the former group are thallous, vanadous, chromous, and ferrous ions. Lamb and Elder† have recently made an extensive study of the depolarizing action of the ferrous-ferric system on the oxygen electrode with particular emphasis on the accelerating

* C. J. Brockman, "Electro-Organic Chemistry," p. 11, John Wiley & Sons, Inc., New York, 1926.

† A. B. Lamb and L. W. Elder, *J. Am. Chem. Soc.*, **53**, 137 (1931).

and narcotic effects of secondary agents. They found that the oxidation of ferrous sulfate by atmospheric oxygen was accelerated by the presence in the solution of copper ions, coconut charcoal, platinum black, and sodium pyrophosphate. The most satisfactory depolarizing solution has the composition 1.1c ferrous sulfate, 0.9c sulfuric acid and at the same time a concentration of charcoal equal to 10 g. in 50 cc. of solution. The potential of the oxygen electrode in this solution is 0.659 v. (reversible oxygen standard potential is 1.2 v.) and the potential falls only to 0.606 v. as a current of density 2,150 ma. per 100 square centimeters flows through the cell. Phenyl urea, amyl alcohol, and acetanilide reduce the efficiency of copper ions and charcoal catalysts in the ferrous sulfate solutions.

Many organic substances may be used as anodic or cathodic depolarizers. The example of acetylene at the anode has already been given. The electrolytic hydrogen given off at the cathode can be added to the organic compound or it can be used to remove oxygen. An example of both of these possibilities is the reduction of nitrobenzene to form aniline. In this reaction oxygen is removed from the nitrobenzene and is replaced by hydrogen,

$$C_6H_5NO_2 + 6H \rightarrow C_6H_5NH_2 + 2H_2O.$$

The speed with which a depolarizer acts is of great importance. If the current density is increased to such a point that the hydrogen and oxygen are liberated faster than the depolarizer can react with them, the potential will necessarily rise to the decomposition voltage of water.

For details concerning the action of depolarizers, the reader is referred to technical books on electrochemistry.*

* C. J. Brockman, *loc. cit.*; Allmand and Ellingham, "The Principles of Applied Electrochemistry," Edward Arnold & Company, London, 1924. Mantell, "Industrial Electrochemistry," McGraw-Hill Book Company, Inc., New York, 1931. M. de Kay Thompson, "Applied Electrochemistry," The Macmillan Company, New York.

CHAPTER XXIX

QUANTUM MECHANICS AND ELECTROCHEMISTRY

It is fitting to close this book with a description of a recent development in theoretical electrochemistry, *viz.*, the application of the principles of the quantum mechanics to various phases of electrochemistry. Quantum mechanics may be invoked for the purpose of giving us a detailed picture of the mechanism by which electrode potentials are set up, or it may be called upon to explain the abnormal mobility of the hydrogen and hydroxyl ions in water. Quantum mechanics has also been applied in theoretical treatments of overvoltage. Other applications of the quantum mechanics to electrochemistry will no doubt be forthcoming in the future. Let us consider first the application of the quantum mechanics to theories of electrode potentials.

Quantum Mechanics and Electromotive Force.—Hitherto in this book we have been content to deal with quantities which can be measured in the laboratory in so far as e.m.f. cells are concerned. Most of our theoretical treatment has been of an exact thermodynamic nature, we have made no speculations concerning the manner in which electrode potentials are produced. Indeed we have not even made an attempt to state at which particular phase boundary the main part of the e.m.f. of a galvanic cell is located. This particular question, the question concerning the location of the potential developed in an e.m.f. cell, has been a subject of great controversy from the days of Volta to the present time.*

Let us consider the well known Daniell cell (Fig. 1) composed of a copper electrode dipping into a solution of copper sulfate and of a zinc electrode dipping into a solution of zinc sulfate, the two solutions assumed to be connected by some sort of a junction which will practically eliminate the very small potential occurring

* For a recent paper on this question see M. de Kay Thompson, *Trans. Electrochem. Soc.*, **63**, 113 (1933), and discussion by Godsey, Fink, Dole, Robinson, and Hutchisson.

at the solution junction. If the concentrations of the two solutions are such that $m_i\gamma_i$ in each case is equal to unity, the net e.m.f. of the cell as measured at the point A is the difference between the standard electrode potentials of zinc and copper, or 1.1 v. Does this e.m.f. of slightly more than a volt occur at the metallic junction between the zinc and copper (Volta p.d.), does it arise from the interface potentials between the zinc and the zinc sulfate solution and between the copper and the copper sulfate solution or is it a combination of both of these types of potentials? Without taking space here for a historical survey* of this "Volta potential difference controversy" so-called, let us see how the quantum mechanics† answers these questions.

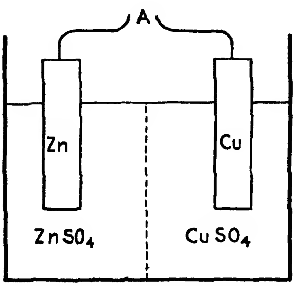


Fig. 1.—The Daniell cell.

We are indebted to Gurney for the first application of the principles of quantum mechanics to electrochemistry.‡ In order to understand his ideas it is first necessary to review briefly several fundamental concepts of modern physics. In considering the vacuum tube as an amplifier, oscillator, and rectifier, we have already become familiar with the thermal emission of electrons. By methods which need not be described here it is possible to determine the work which must be added to a system in order to remove an electron thermally. This quantity or rather a quantity related to it, called the "thermionic work function," is denoted by ϕ, and is the effective potential jump through which the electron passes as it leaves the surface. The thermionic work function for clean, outgassed platinum surfaces has been very carefully determined by two methods by DuBridge§ and found to be 6.27 v.

* See I. Langmuir, *Trans. Amer. Electrochem. Soc.*, **29**, 125 (1916), for an excellent historical review of this question.

† Langmuir, *loc. cit.*, and J. A. V. Butler, *Trans. Faraday Soc.*, **19**, 729 (1924), anticipated much of the treatment which is here presented in the language of the quantum mechanics.

‡ R. W. Gurney, *Proc. Roy. Soc.*, A **134**, 137 (1931); A **136**, 378 (1932); R. H. Fowler, *Trans. Faraday Soc.*, **28**, 368 (1932).

§ L. A. DuBridge, *Phys. Rev.*, **31**, 236 (1928); **32**, 961 (1928).

Electrons may also be ejected from metals by means of light, the so-called *photoelectric effect.* Not light of any frequency will cause the emission of electrons, however; only light having a frequency equal to or in excess of a certain "threshold" value is able to produce this effect. From the threshold value of the frequency, it is possible to calculate the energy required to remove the electron, $h\nu_0$, and from this the work function ϕ by the simple relation

$$\phi\epsilon = h\nu_0. \tag{1}$$

In Eq. (1) h is Planck's constant, ν_0 is the threshold frequency, and ϵ is the unit charge (in this equation usually taken as unity). DuBridge found for clean, outgassed surfaces of platinum that ϕ as determined by photoelectric measurements is 6.30 v., in very close agreement with the value 6.27 determined by thermionic measurements. Apparently the energy required to remove an electron from platinum is a definite quantity. The work function for sodium has not yet been determined very accurately, but it is known to be in the neighborhood of 2 v. What happens at the metal-metal junction when platinum and sodium, for example, are brought together?

Sommerfeld's theory of metals in conjunction with the Fermi-Dirac statistics and the quantum mechanics enables us to obtain a partial answer, at least, to the above question. In Sommerfeld's theory of metals, the valence electrons are quasi-free; that is, they are wandering about the metal somewhat like molecules in a gas and belong to no metallic atom in particular. The metal atoms are consequently ions and occupy definite positions in the crystal structure of the metals. The electrons have energies all the way from zero up to a certain maximum value. According to the Fermi-Dirac statistics the energy distribution of electrons is not very different at the absolute zero from the distribution at room temperature; hence we have the surprising picture of the electrons dashing about at the absolute zero with energies hundreds of times greater than predicted by the older theories even for very high temperatures. This is explained on the basis of the Pauli exclusion principle which allows only two electrons to be in each cell in "phase" space. The quantum mechanics endows these electrons with wave-like properties, and

the wave function which describes the wave properties is also connected with the probability that the electron is in a certain region of space. Following Gurney, let us represent the electron potential-energy levels in two metals such as sodium and platinum by Fig. 2. In Fig. 2 the horizontal lines represent the energy levels of the electrons in the metals, the distance along these lines in the x-direction has no particular meaning. Increasing values of the ordinate represent increasing energy values. The vertical lines extending above the horizontal lines represent the height of the potential barrier at the surface of the metal, the top of the vertical line is the value of the energy that the electron must

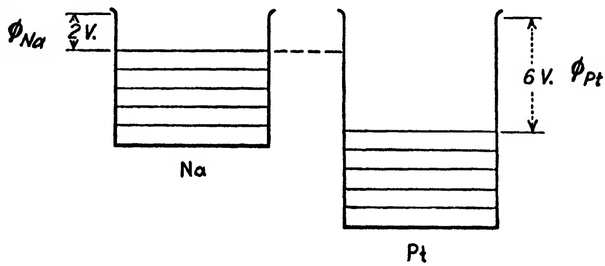


FIG. 2.

have (according to classical notions) in order to escape from the metal. If we bring the sodium and platinum into close contact, there may be a potential barrier formed between the metals which would prevent the electrons from migrating from the sodium to the platinum according to the classical theories of physics, but the newer quantum mechanics tells us that there is always a finite probability of the electron or any particle making a transition between two states of equal energy. Hence electrons will "leak" through the potential barrier from the sodium to the platinum. The loss and gain of electrons will cause the sodium to become positive and the platinum negative until the potential difference is $\phi_{Pt} - \phi_{Na}$, or 4 v. approximately. As a consequence of the transitions of the electrons the energy states will become "leveled up." At equilibrium electrons may make a spontaneous transition between states of equal energy; because the energy states are equal no work will be done on the transfer of the electrons. This is an important point to consider when one remembers that the chief argument

against an appreciable Volta p.d. is that the energy of the cell reaction could be calculated from the e.m.f. (The transfer of electrons between the metals does no work; the work done by the cell must be due to the electrode reactions.)

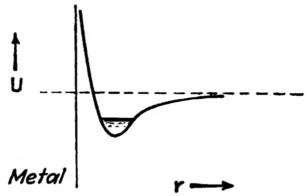


FIG. 3.—Potential-energy curve of a positive ion moving perpendicularly to the metal surface.

Let us now leave our consideration of electrons and turn our attention to positive ions. When a positive ion is removed from a metal or when a positive ion goes into solution, it must do work against the net attraction of the electrons and other ions in the metal (the "mirror-image" forces). Very close to the metal or perhaps just at the metal surface the forces are repulsive, but these repulsive forces fall off very rapidly as the distance from the metal increases and soon give way to the attractive forces mentioned previously. The latter also decrease as the distance increases so that the potential-energy curve of a positive ion along a line perpendicular to the metal surface has the form, in general, of Fig. 3. The horizontal lines in the "dip" of the curve represent possible vibration-rotation energy levels, but in the following we shall ignore levels other than the normal level. As a positive ion approaches a water molecule, it polarizes the water molecule (*i.e.*, it induces a temporary electric moment in the water molecule; see Chap. XII) and is, therefore, attracted to the water molecule or water molecules until, at very close distances, the repulsive forces become effective. Therefore, the potential-energy curve of the positive ion near a water molecule must be of the form illustrated in Fig. 4.

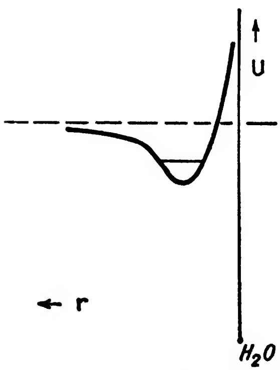


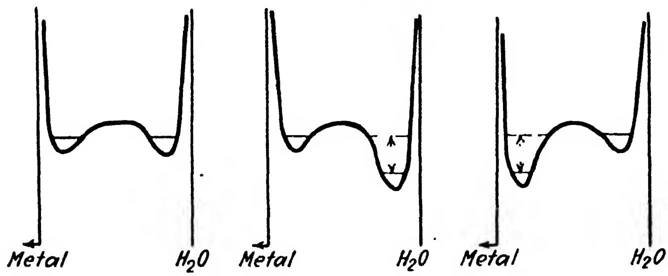
FIG. 4.—Potential-energy curve of a positive ion in the neighborhood of a water molecule.

Quantum mechanics tells us that positive ions can make spontaneous transitions from the surface of the metal to the solution and vice versa despite the existence of a potential barrier at the surface of the metal. Let us consider a single positive ion.

There is a finite probability of finding this ion in the solution. Let us suppose that it leaves the metal surface and makes a jump to the solution. If it does not make an inelastic collision in the solution, it will have enough energy to get back to the metal, but the chances are very great that the ion will lose some of its energy by colliding with a water molecule, and in this way be trapped in the potential-energy "pocket" in the neighborhood of the water molecule. It will accordingly stay in the solution; this is the mechanism by which an ion makes a metal to solution transfer. Not all ions on the metal surface can make transitions; the possibility of a transition taking place is based on the existence of a lower energy level in the solution. If the energy level in the solution that the ion must jump to is higher than the level which the ion occupies in the metal, the metal cannot make the transition. The reverse transition would take place, however. Actually, both transitions occur all the time until equilibrium is attained, when the number of ions depositing becomes equal to the number of ions dissolving. The possibility of ions depositing or dissolving can be illustrated by Figs. 5*a*, 5*b*, and 5*c*. These figures are obtained by uniting Figs. 3 and 4; or rather, by bringing the water molecule close to the metal surface. The curves of Figs. 3 and 4 will then overlap giving three types of potential curves illustrated in Fig. 5. In the case of Fig. 5*a* the normal levels are at the same potential-energy height; hence the transitions of the ions in either direction are in equilibrium and the transitions take place reversibly. In the case of Fig. 5*b* transitions will take place only from the metal to the solution, and these transitions are irreversible because the ions are not able to make spontaneous transitions from a lower energy level to a higher energy level. As the ions leave the metal, the metal becomes negative, with the result that the energy levels are shifted in such a direction that the equilibrium situation represented in Fig. 5*a* is attained. An interfacial potential is set up during this adjustment. In the case of Fig. 5*c*, ions will deposit on the metal shifting the levels and producing an opposite potential, the metal becoming positive.

When two metals which are dipping into solutions of their ions are brought into metallic contact as in the Daniell cell (Fig. 1), the electrons will pass from their high-energy levels in

the zinc metal to lower levels in the copper, thereby lowering the electron levels in the zinc and raising the electron levels in the copper. But the lowering of the electron levels in the zinc means a rise in the positive ion levels in the zinc. This disturbs the equilibrium condition at the metal surface as represented by Fig. 5*a* and produces the situation represented by by Fig. 5*b*, only in this case the difference in potential-energy levels becomes more pronounced. The situation in the copper is just reversed, the electron levels are raised, the ion levels are lowered, and at the metal surface the situation of Fig. 5*c* results. When the current flows, the electrons at the copper-zinc junction flow between levels of equal energy so there is no gain or loss



(*a*) (*b*) (*c*)

FIG. 5.

of energy at this point. At the metal surfaces the ions pass from a high level to a low level; hence the energy of the cell comes from the chemical reaction at the electrodes, *although the differences in positive ion levels at the metal-solution junctions are due primarily to the difference in the electron work functions of the two metals.* Nernst ascribed the electromotive force series of the elements to the difference in the ability of the metals to throw off positive ions, the more active elements such as the alkalies having a greater tendency to give off positive ions to the solution than the more noble metals. In the words of Gurney, "On the contrary, it seems to be the electrons at the metal-metal junction which are responsible, the order of the metals being that of the Volta series."

In concluding this discussion of the Gurney theory of the metallic electrode potential, it should be emphasized that it is impossible to determine the potential at a single interface experi-

mentally; hence the magnitude of the potential as theoretically predicted by any theory cannot be experimentally verified.

Statistical Mechanics and the Glass Electrode.—The above discussion of the application of the quantum mechanics to electrode potential theory has been entirely qualitative, but it is possible to treat interfacial potentials quantitatively. As an example of a mathematical application of the quantum mechanics or rather of statistical mechanics, since we are not concerned here with electrons, let us consider the statistical mechanical theory of the glass electrode.*

The hydrogen electrode function of glass may be explained according to this theory by imagining the hydrogen ion making transitions from its position of equilibrium in the neighborhood of a water molecule in the solution to a position of equilibrium on the surface of the glass; this latter position of equilibrium being at a level of equal or lower potential energy than the level in the solution. While some hydrogen ions are depositing on the glass, *i.e.*, making *d*-transitions, other hydrogen ions on the surface of the glass having high enough energies will be dissolving, *i.e.*, making *s*-transitions. At equilibrium the number of *s*-transitions must equal the number of *d*-transitions, and to obtain an equation for the interfacial potential it is only necessary to write down the number *s*- and *d*-transitions and equate the two quantities. Let $U_{H}^{\circ g}$ be the energy of the lowest quantum level of the hydrogen ion on the glass surface, $U_{H}^{\circ s}$ the energy of the lowest quantum level of the hydrogen ion in the aqueous solution, $U_{Na}^{\circ g}$ and $U_{Na}^{\circ s}$ similar quantities for the sodium ion. We shall now suppose that owing to the interaction of neighboring molecules all energies above the ground level are possible vibration levels, in other words, all values of U between U° and infinity are possible. We shall also assume for the moment that the distribution of the surface ions in their vibration levels is given by the Boltzmann law.

We shall first calculate the number of *s*-transitions or rather the number of *s*-situations which is the number of situations or configurations that gives rise to an *s*-transition. Of the total number of surface ions per unit area of the glass, a fraction

* M. Dole, *J. Chem. Phys.*, **2**, December, 1934. This treatment is typical of Gurney's methods.

$$\frac{1}{kT} \exp\left\{\frac{(U_{\mathrm{H}}^{og} - U)}{kT}\right\} dU \tag{2}$$

will have energies between U and $U + dU$ providing no interfacial potential exists. If an interfacial potential ψ does exist, the energy levels on the glass surface will be shifted relatively to those of the solution by the amount $\epsilon\psi$, where ϵ is the unit positive charge. Taking the potential of the electrolyte as the zero of potential, expression (2) becomes

$$\frac{1}{kT} \exp\left\{\frac{(U_{\mathrm{H}}^{og} + \epsilon\psi - U)}{kT}\right\} dU. \tag{3}$$

The number of s-situations will also be proportional to N_W, the number of water molecules in contact with unit area of surface,

$$\frac{N_W}{kT} \exp\left\{\frac{(U_{\mathrm{H}}^{og} + \epsilon\psi - U)}{kT}\right\} dU. \tag{4}$$

However, part of the surface may be covered by sodium ions; this has the effect of diminishing the number of s-situations for the hydrogen ion. If we let γ represent the fraction of unit surface covered by hydrogen ions, the number of s-situations now is

$$\gamma \frac{N_W}{kT} \exp\left\{\frac{(U_{\mathrm{H}}^{og} + \epsilon\psi - U)}{kT}\right\} dU. \tag{5a}$$

Similarly, the number of s-situations for the sodium ions is

$$(1 - \gamma) \frac{N_W}{kT} \exp\left\{\frac{(U_{\mathrm{Na}}^{og} + \epsilon\psi - U)}{kT}\right\} dU. \tag{5b}$$

The number of d-situations depends upon the number of ions in the solution N_{H} or N_{Na} and upon the energy of the ions; thus for the hydrogen and sodium ions we have

$$\frac{N_{\mathrm{H}}}{kT} \exp\left\{\frac{(U_{\mathrm{H}}^{os} - U)}{kT}\right\} dU, \tag{6}$$

and

$$\frac{N_{\mathrm{Na}}}{kT} \exp\left\{\frac{(U_{\mathrm{Na}}^{os} - U)}{kT}\right\} dU. \tag{7}$$

At equilibrium the number of s-situations multiplied by the probability of a s-transition must be equal to the number of d-situations multiplied by the probability of a d-transition. If the ratio of the latter probability to that of the former be β, then

$$\gamma\frac{N_W}{kT}\exp\left\{\frac{(U_{\mathrm{H}}^{o\varphi}+\epsilon\psi-U)}{kT}\right\}dU=\beta\frac{N_{\mathrm{H}}}{kT}\exp\left\{\frac{(U_{\mathrm{H}}^{os}-U)}{kT}\right\}dU \qquad (8a)$$

$$(1-\gamma)\frac{N_W}{kT}\exp\left\{\frac{(U_{\mathrm{Na}}^{o\varphi}+\epsilon\psi-U)}{kT}\right\}dU=$$
$$\beta_{\mathrm{Na}}\frac{N_{\mathrm{Na}}}{kT}\exp\left\{\frac{(U_{\mathrm{Na}}^{os}-U)}{kT}\right\}dU. \qquad (8b)$$

Letting Q_{H} equal $(U_{\mathrm{H}}^{os}-U_{\mathrm{H}}^{o\varphi})$ and Q_{Na} equal $(U_{\mathrm{Na}}^{os}-U_{\mathrm{Na}}^{o\varphi})$ and setting N_{H}/N_W and N_{Na}/N_W equal to c_{H} and c_{Na}, respectively, Eqs. (8a) and (8b) become

$$\gamma=c_{\mathrm{H}}\beta_{\mathrm{H}}\exp\left\{\frac{Q_{\mathrm{H}}-\epsilon\psi}{kT}\right\} \qquad (9a)$$

and

$$(1-\gamma)=c_{\mathrm{Na}}\beta_{\mathrm{Na}}\exp\left\{\frac{(Q_{\mathrm{Na}}-\epsilon\psi)}{kT}\right\}. \qquad (9b)$$

The quantity "γ" is easily eliminated from Eqs. (9a) and (9b) by addition; we obtain

$$c_{\mathrm{H}}\beta_{\mathrm{H}}\exp\left\{\frac{(Q_{\mathrm{H}}-\epsilon\psi)}{kT}\right\}+c_{\mathrm{Na}}\beta_{\mathrm{Na}}\exp\left\{\frac{(Q_{\mathrm{Na}}-\epsilon\psi)}{kT}\right\}=1. \qquad (10)$$

If there were no sodium ions present in the solution, the potential would depend solely on the concentration of hydrogen ions; from Eq. (10) we have, on setting c_{Na} equal to zero

$$\psi_{\mathrm{H}}=\frac{Q_{\mathrm{H}}}{\epsilon}+\frac{kT}{\epsilon}\ln c_{\mathrm{H}}\beta_{\mathrm{H}}. \qquad (11)$$

Equation (11) is the usual hydrogen electrode potential equation since β_{H} is a factor of the order of magnitude of unity. The author originally defined the "error of the glass electrode" as being equal to $\psi-\psi_{\mathrm{H}}=\Delta E$ (see Chap. XXV). This quantity may be obtained by dividing Eq. (10) (first putting Eq. (11) in its exponential form) by Eq. (11) and rearranging, the result being

$$\Delta E = \psi - \psi_{\mathrm{H}} = \frac{kT}{\epsilon} \ln \left\{ \frac{\frac{\beta_{\mathrm{Na}}}{\beta_{\mathrm{H}}} e^{\frac{(Q_{\mathrm{Na}} - Q_{\mathrm{H}})}{kT}} c_{\mathrm{Na}} + c_{\mathrm{H}}}{c_{\mathrm{H}}} \right\}. \tag{12}$$

Equation (12) is interesting inasmuch as it has been shown that an equation similar to Eq. (12) is applicable to the glass electrode. In order for Eq. (12) to reproduce accurately the experimental results it is only necessary to assume reasonable values for $Q_{\mathrm{Na}} - Q_{\mathrm{H}}$. However, it is impossible at the present time to estimate $Q_{\mathrm{Na}} - Q_{\mathrm{H}}$ theoretically, so that we must leave this subject with the statement that Eq. (12) is consistent with the observed facts but cannot be rigorously tested.*

Quantum Mechanics and Overvoltage.—An interesting application of the quantum mechanics to the explanation of overvoltage has been carried out by Gurney.† Gurney's theory has also been extended by Bell‡ in a theory for the electrolytic separation of the isotopes of hydrogen.

In the first section of this chapter we have considered the quantum mechanical principles involved in the solution and deposition of a positive ion, *i.e.*, the passage of a positive ion from its position in the metal lattice to the solution and *vice versa.* Here we shall discuss hydrogen and oxygen overvoltage, and since in this case we have to deal with the neutralization of an ion to form a neutral substance, the treatment will necessarily be somewhat different.

We are concerned with the passage of electrons through the potential barrier at the surface of the electrode rather than with the passage of ions. The general idea of Gurney's theory is that an overvoltage must exist in order that enough electrons can slip through the potential barrier at the metal surface to constitute a current of appreciable magnitude. As the potential at the cathode, for example, rises, the electron energy levels at the cathode are raised, so that more electrons are available for neutralizing the hydrogen ions that approach the cathode,

* Equation (12) may be tested to a certain extent by measuring the temperature coefficient of the glass electrode. Unpublished data obtained by Miss Charlotte Erwin in the author's laboratory indicate that Eq. (12) reproduces the error of the glass electrode at 50°C. with fairly good accuracy.

† R. W. Gurney, *Proc. Roy. Soc.*, A **134**, 137 (1931).

‡ R. P. Bell, *J. Chem. Phys.*, **2**, 164 (1934).

and a large current can flow through the cell. Since the distribution of electron energy levels in metals over a limited range follows an exponential law, any increase in these levels due to an applied e.m.f. increases the current exponentially.

Let us consider the neutralization of a hydrogen ion as it approaches the cathode. According to the quantum mechanics it is not necessary that the hydrogen ion come into actual contact with the electrode to be neutralized; electrons from the platinum can slip through the potential barrier to the ion even if the ion is several molecular diameters away from the electrode.

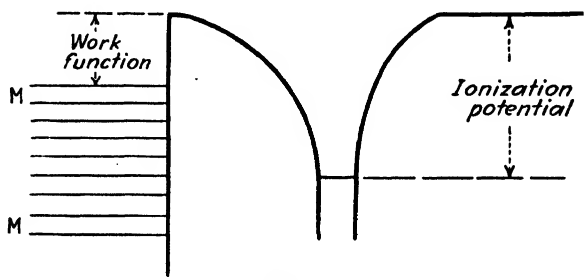


FIG. 6.

Such a transfer of electrons, however, cannot occur unless the energy released on neutralization is greater than the energy necessary to remove the electron from the metal (the work function $\phi\epsilon$ of the metal). This is illustrated by Fig. 6, where *MM* represent occupied electron energy levels in the metal, and the curves represent the potential energy of an electron along a line perpendicular to the surface of the metal. The single electron level to the right shows the energy that the electron has after neutralizing the ion, and as this level is lower than occupied levels in the metal, the electron can make the transition, metal to ion, spontaneously. If the ionization potential of the atom happens to be small, the electron levels in the metal will be lower than the unoccupied electron level in the ion so that neutralization of the ion will be impossible. This explains the fact mentioned in Chap. XIII that cesium ions can exist on tungsten filaments without being neutralized.

Figure 6 actually represents the case for a gaseous positive ion rather than for an ion in solution, because in solution the ion

is hydrated, and since it has lost energy in the act of hydration, the ionization potential has been modified accordingly. When a hydrated ion is neutralized, some energy must be absorbed to dehydrate the ion, so to speak. The net amount of energy liberated on neutralization, is, therefore, less by the amount of energy of dehydration. This means that there is a possibility that some ions in the hydrated condition cannot be neutralized at the electrode by a spontaneous transition of an electron, although in the unhydrated condition they would be neutralized. Figure 7 illustrates just such a case for a positive ion; neutralization could have taken place in a gas or vacuum but is impossible in solution since there are no electrons in the metal having energies high enough to make the transition. Figure 8 represents a similar situation for a negative ion. In Fig. 7, $E\epsilon$ (ϵ is the unit charge; potential difference multiplied by charge is energy) represents the energy liberated on neutralization, and as this is less than the energy necessary to liberate an electron from the

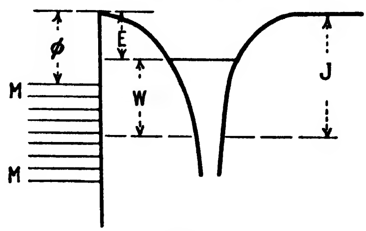


FIG. 7.

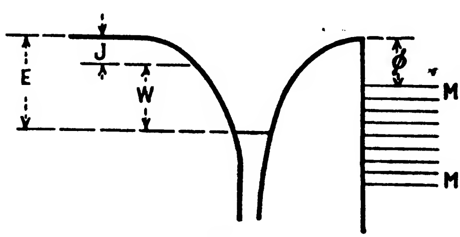


FIG. 8.

metal, the ion cannot be neutralized. $W\epsilon$ is the energy of hydration, and if J is the ionization potential, the neutralization potential E (not to be confused with E meaning e.m.f. of a galvanic cell). for positive and negative ions is given by the equations

$$E_+ = J_+ - W_+$$
$$E_- = J_- + W_-. \tag{13}$$

The necessary condition for neutralization of an ion in solution is

$$E_+ > \phi$$
$$E_- < \phi \tag{14}$$

where ϕ is the work function of the metal.

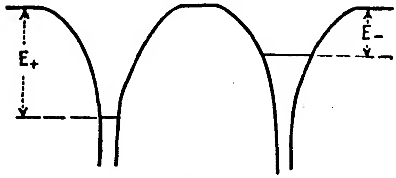


FIG. 9.—$E_+ > E_-$. The ions would spontaneously neutralize each other.

It might occur to the reader that a situation could exist where the neutralization potentials of both positive and negative ions simultaneously fulfilled conditions in Eq. (14); if such a situation did exist, electrolysis could proceed without applying any external e.m.f. However, it is impossible for the negative ion to have a lower neutralization potential than the positive ion; for if this were so, electrons from the negative ions in solution could filter across to the positive ions and spontaneously neutralize them. We know that in the case of strong electrolytes we can have large numbers of positive and negative ions existing together; hence E_+ must be less than E_-. These relationships are expressed in Figs. 9 and 10.

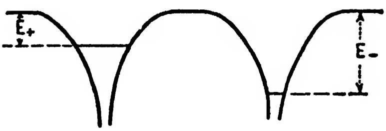


FIG. 10.—$E_+ < E_-$. Ions can exist in solution.

To bring about electrolysis, it is evident that ϕ must be reduced at the negative electrode and increased at the positive electrode because E_+ and E_- are fixed quantities. If E_+ is less than ϕ and must be greater than ϕ for electrolysis to occur, we must reduce ϕ by applying a potential until E_+ becomes greater than ϕ. A moment's reflection will show that the application of an external e.m.f. does just exactly these things, it effectively lowers ϕ at the cathode and raises it at the anode. The conditions for electrolysis are therefore,

$$E_+ > \phi - V_c \tag{15}$$
$$E_- < \phi + V_a$$

where V is the overvoltage.

On the basis of these fundamental ideas Gurney has been able to calculate the variation of the overvoltage with variation of the electrolysis current and obtains good agreement with the data.

Quantum Mechanics and Electrical Conductance.—Bernal and Fowler have recently presented an interesting (although not entirely perfected) explanation of the abnormally high mobility of the hydrogen and hydroxyl ions in water. Under an applied electric field of 1 v. per centimeter at room temperature most ions such as the potassium, chloride, etc., ions move through water with a velocity of 6.7×10^{-4} cm. per second, while the hydrogen ion moves nearly five times as fast, 32.5×10^{-4} cm. per second. The hydroxyl ion moves at the rate of 17.8×10^{-4} cm. per second. This mobility of the hydrogen ion is all the more surprising when it is realized that the proton cannot exist unhydrated in water. All evidence points to the fact that the hydrogen ion is $(OH_3)^+$, an ion whose size is apparently about the same as that of the potassium or ammonium ion. The $(OH_3)^+$ ion may be more or less hydrated in the same way that other ions are hydrated. The structure of the simple $(OH_3)^+$ ion is probably like that of ammonia (see Chap. XII).

Bernal and Fowler's* line of reasoning is based on the fundamental principles of the quantum mechanics which we have discussed above. If an $(OH_3)^+$ or hydrogen ion is in sufficiently close contact with a neighboring water molecule, the extra proton on the hydrogen ion can "leak" through the potential barrier to a position of equal energy on the neighboring water molecule. Of course, the proton has a far greater mass than the electron and the probability of its transfer will be correspondingly far less, nevertheless it will be possible for the proton to make these jumps since the potential barrier between the proton and the neighboring water molecule may be very slight or even nonexistent provided that the hydrogen ion and the water molecule are properly oriented with respect to each other. In the absence of an applied electric field, we can picture the proton as making transitions from water molecule to water molecule more or less at random, but having no net motion in any direction. When the field is applied, there will be a slightly greater probability that the proton will make a transition in the direction of the

* J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933). See, however, Bernal, *Trans. Faraday Soc.*, **30**, 787 (1934).

field. Thus when a hydrogen ion and neighboring water molecule are in a position favorable for the transfer of the proton, the proton will very likely be found attached to the water molecule lying in a region of lower potential energy for the proton when the favorable conjunction is broken. A region of lower potential energy will be a region farther down the potential gradient. In this way the applied field will cause a certain drift of the protons in the direction of the field. Of course, the hydrogen ion itself will move bodily through the solution at a speed about equal to that of the ammonium ion probably, but it is the extra preferred drift of the protons which accounts for the abnormally high mobility of the hydrogen ion.

In the case of the hydroxyl ion, let us quote Bernal and Fowler, "A very similar mechanism must hold for $(OH)^-$. In a favorable conjunction of $(OH)^-$ and another OH_2, a proton can pass from OH_2 to the $(OH)^-$ and the systems can separate again with the ion and neutral system interchanged. But it is clear that the two H's in OH_2 will lie slightly deeper in the electronic system than the three H's in $(OH_3)^+$ and have therefore somewhat less chance of making the exchange. Hence the smaller mobility."

As stated in Chap. I, this proton transfer theory bears a close resemblance to the old Grothuss chain theory of ionic conduction. However, in the case of ions of greater mass than the proton, the probability of transition through potential barriers becomes too small to be of importance in conduction. Indeed Bernal and Fowler point out that the $(H^2)^+$ ion (ion formed from deuterium, the isotope of hydrogen) may be expected to have a practically normal mobility.

Bernal and Fowler find it necessary to demonstrate the existence of a coordinated structure in water in order to account for the high mobility inasmuch as calculations show that if water is a close packed structure of freely rotating molecules, the number of favorable orientations would not be sufficient to account for the abnormal mobility of the hydrogen ion. Their quantitative calculations carried out as accurately as possible considering all the uncertainties involved indicate that the proton-jump theory gives a reasonable explanation of the observed mobilities.

The abnormally rapid increase in electrical conductance with increase of concentration of solutions of sodium dissolved in ammonia is given an explanation by Farkas* on the basis of the principles of quantum mechanics. In this case one has to deal with a situation quite similar to the one concerning the aqueous conductance of the hydrogen and hydroxyl ions treated by Bernal and Fowler. Electrons "leak" through the potential barriers from one sodium atom to another, the net drift of the electrons will be in the direction of the applied field (with sign allowed for). The sodium atoms must be assumed to be oriented favorably with respect to one another; the necessity for this orientation gives rise to the marked dependence of the conductance upon the concentration. Fair agreement between theory and data is obtained by selecting a favorable value for the ionization potential of the sodium atoms dissolved in liquid ammonia.

* L. Farkas, *Z. physik. Chem.*, **A 161**, 355 (1932).

APPENDIX

A LIST OF THE CHIEF SYMBOLS USED

TOGETHER WITH THE CHAPTER NUMBERS WHERE THE SYMBOLS ARE FIRST DEFINED

A	Cross-sectional area, III.
	Constant of various equations.
a	Acceleration, V.
$\mathbf{a}$	Distance between centers of ions (ion diameter), II.
B	Constant of various equations.
b	Radius of ion, VI.
C	Degrees centigrade, II.
	Capacitance, IV.
c	Moles per liter of solution, II.
	Velocity of light, XII.
D	Dielectric constant, II.
d	Density, XII.
E	Electric potential difference, either e.m.f. or p.d., always a measurable quantity, III.
	Neutralization potential (not a measurable quantity), XXIX.
E_d	Decomposition voltage, XXVIII.
$\mathbf{E}$	Electric field strength or intensity, III, XII.
E°	Standard electrode potential when $m\gamma = 1$, XVI.
$\mathbf{E}^\circ$	Standard electrode potential when $cf = 1$, XXIII.
e	Base of the natural (Napierian) logarithms.
exp( )	e to the power ( ).
F	The faraday, III.
$\mathbf{F}$	Electric intensity, XII.
f	Force, II.
	Frequency, IV.
	Activity coefficient defined in terms of the mole fraction, XV.
$\mathbf{f}$	Activity coefficient defined in terms of moles per liter of solution, XVII.
G	Free energy (ΔG, at constant pressure, is positive when G of system increases), XV.
g	Landé factor, XIII.
	Gravitational acceleration in dynes, XXVII.
H	Magnetic-field strength, XIII.
	Heat content (ΔH is positive when H of system increases), XV.
h	Planck's constant, XIII.

I	Electric current, III.
$\mathbf{I}$	Electric moment per unit volume, XII.
i	Van't Hoff factor, II.
$\mathbf{i}$	Current density, III.
J	Joules, III.
	Resultant of S and L, XIII.
	Ionization potential, XXIX.
j	Operator, IV.
K	Thermodynamic L.M.A. constant, XV.
	Degrees absolute.
K_c	Classical L.M.A. constant, II.
$K_{acid.}$, $K_{bas.}$	Brønsted acidity and basicity constants, XX.
K_h	Hydrolysis constant, XXI.
k	Friction constant, V.
	Gas constant per molecule (Boltzmann's constant), VI.
L	Inductance, IV.
	Resultant of M_l's, XIII.
	Solubility product constant, XXIV.
l	Length, III.
M	Molecular weight, XII.
	Magnetic quantum number, XIII.
m	Moles per 1,000 g. of solvent, II.
	Mass, IV.
	Temporary electric moment, XII.
N	Normality (equivalents per liter of solution), IV.
$\mathbf{N}$	Avogadro's number, V.
$\mathcal{N}$	Mole fraction, XV.
n	Number of moles, II.
	Total number of ions resulting from the dissociation of one molecule, II.
	Number of ions per cubic centimeter, V.
	Number of dipoles per unit volume, XII.
$\mathbf{n}$	Unit vector, XII.
P	Osmotic pressure, II.
	Pressure.
	Molal polarization, XII.
P^*	Fugacity of a gas, XV.
p	Vapor pressure, XV.
p^*	Fugacity of solute, XV.
Q	Charge on condenser, XI.
	Energy difference constant, XXIX.
q	Charge on particle, II.
	Heat gained by system, XV.
R	Perfect gas law constant, II.
	Electric resistance, III.
r	Distance, II.
S	Resultant of M_s's, XIII.

	Entropy (ΔS is positive when S of system increases), XV.
s	Length, III.
	Number of equivalents, IX.
T	Absolute temperature, II.
t	Centigrade temperature, II.
	Transference number, IX.
U	Potential energy, II.
	Internal energy (ΔU is positive when U of system increases), XV.
u	Mobility of positive ion, V.
V	Volume.
v	Mobility of negative ion, V.
$\bar{v}$	Actual velocity, V.
W	Hydration potential, XXIX.
w	Work done by system, XV.
	Molecular weight of solvent, XVI.
X	Electric field strength in the x-direction, III.
	Reactance, IV.
Z	Impedance, IV.
z	Valence of ion (always to be taken as positive unless stated to the contrary), V.
α (alpha)	Degree of dissociation, II.
	Overvoltage constant, XXVIII.
α_0	Polarizability, XII.
β (beta)	Probability ratio, XXIX.
Γ (gamma)	Surface concentration (moles per square centimeter), XXVII.
γ	Activity coefficient defined in terms of moles per 1,000 grams of solvent, XVI.
	Surface or interfacial tension, XXVII.
	Fraction of surface, XXIX.
ϵ (epsilon)	Elementary charge of electricity (always positive unless stated to the contrary), VI.
ζ (zeta)	"Zeta" or electrokinetic potential, XXVI.
η (eta)	Viscosity, V.
θ (theta)	Relaxation time, VII.
	Angle, XII.
κ (kappa)	Specific conductance, III.
	Debye-Hückel quantity, VI.
Λ (lambda)	Equivalent conductance, IV.
$\bar{\Lambda}$	Molal conductance, IV.
Λ_e	Defined by Eq. (35), Chap. V.
μ (mu)	Permanent electric moment, XII.
	Magnetic moment, XIII.
	Chemical potential, XV.
	Ionic strength, XVII.
$\bar{\mu}$	Electrochemical potential, XXII.
μ_i°	Chemical potential of component when $N_i f_i = 1$, XV.

μ_i°	Chemical potential of component when $c_i \cdot f_i = 1$, XXII.
ν (nu)	Number of ions of one kind that one molecule dissociates into, V.
	Frequency of light, XXIX.
Π (pi)	Volume density of charge, XVIII.
π	Ratio of circumference to diameter of circle.
ρ (rho)	Friction coefficient, VI.
Σ (sigma)	Summation symbol.
σ	Surface density of charge, XII.
τ (tau)	Time in seconds, III.
Υ (upsilon)	Maximum number of dissolved ions per square centimeter of interfacial surface, XXVII.
Φ (phi)	Specific adsorption potential, XXVII.
	Work function, XXIX.
φ	Fluidity, VI.
ψ (psi)	Electric potential (not measurable), III.
Ω (omega)	Surface area, XXVII.
ω	Angular velocity ($= 2\pi f$ where f is the frequency), IV.

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